Physical Chemistry

Experimental testing of molecular dynamic functions of pairs by the isotope selectivity of radical recombination

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A method for experimental testing of the molecular dynamic function $f(t)$, which describes the generation of reencounters in a dynamic pair of molecular particles, has been developed. The method is based on the analysis of isotope separation in spin selective reactions of a radical pair. The $f(t)$ function derived from the solution of the diffusion equation with physically rigorous initial and boundary conditions describes experimental results much better than the well-known Noyes function. Conditions that make it possible to increase the efficiency of isotope separation in spin selective reactions are formulated.

Key words: radical pair, isotope effect.

A new field of chemistry, spin chemistry, studies the behavior of angular moments (spins) of electrons and nuclei in chemical reactions and effects caused by them. The origin of such effects can be seen in the example of recombination (or disproportionation) of radical pairs in liquids and solid states with allowed diffusion. This reaction is electron spin selective: it is allowed for a singlet state of a pair and forbidden for a triplet state (when the spin is equal to unity). Therefore, the reaction dynamics (measured by the rate constant or the probability of recombination of a pair) depends on the rate of spin transformation of a pair.[1,2]

A radical pair (RP) is a dynamic microreactor, from which radical-partners can leave to perform "diffusion trips" of various duration; they can then return, encounter again, *etc.* This process is described by the molecular dynamic function $f(t)$; it determines the probability that a particle that has left the RP at the initial moment ($t = 0$) will return later to its partner at moment t. The totality of diffusionally controlled events in the RP comprises its molecular dynamics, whose quantitative characteristics comprise the $f(t)$ function. This work is devoted to considering this function.

To the moment of the reencounter of partners the RP should be in a singlet state (if the RP had the initial triplet state) and be ready for recombination. This process of spin transformation is described by the spin dynamics with the $\sin^2(\omega t)$ function as its qualitative expression, where ω is the frequency of triplet-singlet transitions in the RP.

The "chemical survival" of the RP to the t time moment, *i.e.*, the retention of the pair, is also the necessary and evident condition. This condition is provided by the chemical dynamics with the $\exp(-kt)$ function, where k is the decay rate constant of the RP due to decomposition or accepting the radical-partners, *i.e.*, in fact, it is the reverse lifetime of the shortest-lived partner of the RP.

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Thus, the formation of a molecule from the triplet RP is the result of "collective efforts" of three dynamics: molecular, spin, and chemical dynamics. This event can occur in the case when three preceding events coincide in time: the encounter of partners in the RP, the retention of the RP itself (its survival), and, finally, the spin conversion of the RP, *i.e.*, a chance for the RP to be in a singlet state at the instant of the reencounter (t).

The probability of recombination of a triplet RP at the given moment t is the product of probabilities of these three independent events

$$P(t) = f(t) \cdot \sin^2(\omega t) \cdot \exp(-kt). \quad (1)$$

The total probability is the integral value

$$P = \varepsilon \int_0^{\infty} f(t) \cdot \sin^2(\omega t) \cdot \exp(-kt)\mathrm{d}t, \quad (2)$$

which summarizes results of all reencounters of partners for the lifetime of the RP $\tau = k^{-1}$; ε is the recombination cross section of the contact singlet RP, which is ready for recombination. The ε value can vary from zero (a completely reflecting "white" reaction sphere) to unity (a completely absorbing "black" sphere).

It unambiguously follows from Eq. (2) that the probability of molecule formation depends on the frequency of triplet-singlet transitions (ω): this probability is small for the RP with nonmagnetic nuclei (for example, ^{12}C), while it is considerable for the RP with ^{13}C due to the fact that the strong interaction between unpaired electrons and the magnetic nucleus of ^{13}C stimulates the fast triplet-singlet spin conversion of the RP and prepares the pair for recombination more rapidly. For example, in the RP ($PhCH_2{}^{\cdot}\ {}^{\cdot 12}COCH_2Ph$) generated by photolysis of dibenzylketone $\omega = 4.8 \cdot 10^8$ rad s^{-1}, while in the RP ($PhCH_2{}^{\cdot}\ {}^{\cdot 13}COCH_2Ph$) $\omega^* = 22.2 \cdot 10^8$ rad s^{-1}. It follows from Eq. (2) that the second, *i.e.*, "magnetic" (containing ^{13}C), RP recombinates more rapidly than the first, *i.e.*, "nonmagnetic" (with ^{12}C nuclei), RP. As a result, ^{13}C nuclei return to initial molecules more rapidly than ^{12}C ones. Just this difference in reactivity of magnetic and nonmagnetic RP is the nucleus-spin selectivity or the magnetic isotope effect, which sort magnetic and nonmagnetic nuclei in chemical reactions.[3,4]

The effect considered provides the accumulation of the magnetic isotope ^{13}C in initial molecules (for example, in dibenzylketone during its photolysis). The enrichment (S) depends on the chemical conversion (F):

$$\log S = (1 - \alpha_G) \log (1 - F), \quad (3)$$

where α_G (the key value) is the coefficient of one-step isotope separation,

$$\alpha_G = (1 - P)/(1 - P^*), \quad (4)$$

and P and P^* are determined by Eq. (2) for nonmagnetic and magnetic RP with ω and ω^* parameters, respectively.

Thus, the isotope separation in the spin selective reaction of RP recombination is a function of several parameters (k, ω, and ω^*), which are either known or equal for magnetic and nonmagnetic RP. Now it becomes evident that the isotope separation can be used as the experimental testing of the molecular dynamic function $f(t)$, *i.e.*, the function of generating reencounters (repeated contacts) of partners of the RP.

Such an experimental testing $f(t)$ has yet been unsuccessful. Attempts to test $f(t)$ by an example of the pair of iodine atoms photochemically generated from molecular iodine failed, because the dynamics of this pair detected within the picosecond range was complicated due to the energy relaxation of electronically vibrational excited states of I_2 molecules (see Refs. 5 and 6). The purpose of this work is to analyze various $f(t)$ functions and, using experimental data on isotope separation, to choose such an $f(t)$ function that could provide the best agreement with experiment.

Molecular dynamic function of a pair

The $f(t)$ function appeared in the chemical kinetics from analysis of liquid-phase diffusionally limited bimolecular reactions and entered the dynamics of these reactions in three ways. The first of them originates from the ideas of Smoluchowski[7,8] and is based on the solution of equations that determine the diffusion flow of reacting molecules on the surface of the absorbing sphere with the radius R, in the center of which the second reagent is placed. The $f(t)$ function is determined from the concentration gradient at the interface of the sphere with boundary conditions formulated in the known works.[9,10]

The system, which describes this physical situation, includes the following equations:

$$\frac{\partial C}{\partial t} = D\nabla^2 C, \quad (5)$$

$$C(r, 0) = C_0, \quad (6)$$

$$D\left(\frac{\partial C}{\partial r}\right)_{r=R} = bC(R, t). \quad (7)$$

The first (diffusion) equation (Eq. (5)) determines the concentration of particles $C(r, t)$ at the instant time t on the surface of the sphere with the r radius ($r \geq R$), the second equation (Eq. (6)) specifies the initial (uniform) particle distribution, and the third equation (Eq. (7)) determines the boundary condition: the concentration gradient on the sphere surface at $r = R$ is proportional to the concentration on the sphere; D and b are parameters (see below). The final result of the solution of system (5)—(7) is the expression for the rate constant of the bimolecular process:

$$k(t) = k_0[C(R, t)/C_0], \quad (8)$$

in which k_0 (at $t = 0$) and k_{∞} (at $t \to \infty$) serve as testing parameters (for comparing variants of the solution with different boundary conditions).

The system of Eqs. (5)—(7) can be reformulated in another, "probability" variant.[11] Let us introduce the function $w(r, t; r_0, R)$, determining the probability of the fact that a particle, which begins its diffusion motion from point r_0 ($r_0 > R$), is at distance r from the center of the sphere to moment t. Then $4\pi r^2 w(r, t; r_0, R)$ is the probability of the fact that the particle, starting from the point where $r = r_0$ at $t = 0$, reaches the surface of the sphere with radius r at moment t (the point of localization of the first reagent is still the center of the sphere).

Then the behavior of the w function is described by the system of equations:

$$\frac{\partial w}{\partial t} = D\nabla^2 w, \tag{9}$$

$$w(r, t = 0) = (4\pi r^2)^{-1}\,\delta(r - r_0), \tag{10}$$

$$w(r, t) \to 0 \text{ at } r \to \infty, \tag{11}$$

$$D\left(\frac{\partial w}{\partial r}\right)_{r=R} = bw(R, t). \tag{12}$$

The first equation (Eq. (9)) is completely analogous to the diffusion equation (see Eq. (5)), the second equation (Eq. (10)) determines the condition of the start of the particle from the r_0 distance (by the δ function), the third equation (Eq. (11)) specifies the boundary condition at infinity, and the fourth equation (Eq. (12)) specifies the boundary condition on the surface of the reaction sphere at $r = R$ and is similar to Eq. (7). The solution of system (9)—(12) was given[12] in the form

$$\begin{aligned} 4\pi r^2 w(r, t; r_0, R) = {} & \frac{r}{2r_0(\pi Dt)^{1/2}}\{\exp[-(r - r_0)^2/(4Dt)] + \\ & + \exp[-(r + r_0 - 2R)^2/(4Dt)] - \\ & - 2B(\pi Dt)^{1/2}\cdot\exp[B^2 Dt + \\ & + B\,(r + r_0 - 2R)]\cdot\mathrm{erfc}[B(Dt)^{1/2} + \\ & + (r + r_0 - 2R)/(4Dt)^{1/2}]\}, \end{aligned} \tag{13}$$

where $B = b/D + 1/R$; erfc is the error function known in mathematics; $b = \varepsilon u_0/4$; u_0 is the rate of motion of the particle ($u_0 = \nu l$, ν is the frequency of diffusional shifts of the particle, l is the amplitude); and D is the diffusion coefficient.

Dependence (13) is a more general than the $f(t)$ function under consideration. This dependence determines the probability for the particle starting at $t = 0$ from the point with the r_0 coordinate to reach the sphere with the arbitrary r radius at the t moment. The $f(t)$ function specifies the probability of the fact that the particle, starting from the reaction surface with $r_0 = R$, returns to the same surface. The seeming easiness of deriving $f(t)$ from Eq. (13) by substituting the R radius of the reaction surface instead of r and r_0 can be seen immediately.

System (9)—(12) allows one to obtain the function

$$p(t; r_0, R) = 4\pi R^2 D\left(\frac{\partial w}{\partial r}\right)_{r=R}, \tag{14}$$

which is determined as a probability for the particle starting at $t = 0$ from point r_0 (but not from point R, as for the $f(t)$ function!) to find itself on the surface of the reaction sphere of radius R at moment t (see Refs. 13 and 14). Then the $k(t)$ rate constant, as shown previously,[11] can be presented in the form

$$k(t) = 4\pi R^2 b\,[1 - \int_0^t p(t'; r_0 = R, R)\mathrm{d}t']. \tag{15}$$

Thus, it is impossible to obtain the correct $f(t)$ function from Eq. (13) by substituting $r = r_0 = R$ into it, because the boundary conditions (7) and (12) are contradictory, *i.e.*, they imply a break in the gradient of probability density w (or concentration $C(r, t)$) on the reaction sphere surface. Then the diffusion equation, rigorously speaking, is inappropriate, because the constraint of continuity at the boundary with $r = R$ is violated.

The way out of this contradictory situation is suggested in the known work,[15] which also presents the detailed analysis of the problem on diffusion near the boundary of the reaction sphere and on the reaction sphere. The idea is in the fact that the boundary of the start should be shifted to the point with $r_0 = R + \Delta$, *i.e.*, it should be shifted by a small Δ value equal to $(2/3)l$ from the reaction sphere with radius R. Then the boundary condition is determined by the expression:

$$D\left(\frac{\partial w}{\partial r}\right)_{r=R} = bw(R + \Delta, t) \tag{16}$$

instead of Eq. (12).

In this case, the $f(t)$ function can be obtained from general Eq. (13) by substituting $r = R$, $r_0 = R + \Delta$:

$$\begin{aligned} f(t)_{\mathrm{DE}} = {} & \frac{b}{(1 + \Delta/R)}(\pi Dt)^{-1/2}\cdot\exp[-\Delta^2/(4Dt)]\,\times \\ & \times\{1 - B(\pi Dt)^{1/2}\cdot\exp\{[\Delta/(4Dt)^{1/2} + \\ & + B(Dt)^{1/2}]^2\}\cdot\mathrm{erfc}[\Delta/2(Dt)^{1/2} + B(Dt)^{1/2}]\} \end{aligned} \tag{17}$$

(the DE index indicates that $f(t)$ originates from solution of the diffusion equation). Here $B = b/D + 1/R$, $b = \varepsilon u_0/4$, $D = u_0 l/3$, and $u_0 = \nu l$, as previously. To visualize the shape of the $f(t)_{\mathrm{DE}}$ function, let us introduce the following dimensionless parameters: $\tau = 1/\nu$, $2(Dt)^{1/2} = \Delta(3t/\tau)^{1/2}$, $\xi = 2(DT)^{1/2}/\Delta = (3t/\tau)^{1/2}$, and $H(\xi)\mathrm{d}\xi = f(t)_{\mathrm{DE}}\mathrm{d}t$. Here ξ is the dimensionless time measured from its consumption for diffusionally overcoming a Δ path; $H(\xi)$ is the $f(t)_{\mathrm{DE}}$ function reduced to the dimensionless time scale.

The shape of the $H(\xi)$ curve is shown in Fig. 1: the function passes sharply through a maximum near $\xi = 1.5$ and then descends according to the approximate law:

$$H(\xi) \sim (1/\xi^2)\exp(-1/\xi^2). \tag{18}$$

It should be kept in mind that the Fick law and values calculated by this law are rather approximate and

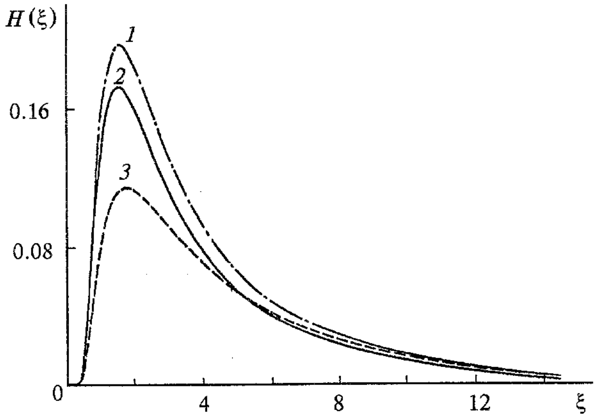

Fig. 1. $H(\xi)$ function at chosen values of ε and Δ/R parameters.[15] Curves: *1*, $\varepsilon = 1$, $\Delta/R = 0.01$; *2*, $\varepsilon = 1$, $\Delta/R = 0.1$; *3*, $\varepsilon = 0.67$, $\Delta/R = 0.1$.

true with accuracy to first terms in power-series expansions for concentrations and diffusion flows. More particularly, it means that all equations are appropriate for $l/R \ll 1$ (for $l/R \approx 0.2$ the accuracy is 4 to 5 %) and for $t \gg \tau$ (for $t \approx (4/3)\tau$ the accuracy of the diffusion equation is higher than 10 %).[15] It is evident that these approximations are very good ones. Their use in practice should not be under doubt (at least for distances of the atomic-molecular scale, and shorter distances are usually insignificant in chemistry).

Recall that the first way of introducing the $f(t)$ function to the kinetics of diffusionally limited bimolecular processes has yet been considered. The second was suggested by Noyes who determined the bimolecular constant by the equation[16,17]

$$k(t) = k_0\,[1 - \int_0^t h(t')\mathrm{d}t], \tag{19}$$

similar to Eq. (15) with the same physical meaning of the $h(t)$ function as $p(t;\ r_0 = R,\ R)$. However, an eigenfunction was used as $h(t)$ (let us call it the Noyes function and designate for universality as $f(t)_{\mathrm{N}}$), which was derived from the model of free chaotic displacements (or flights).[18]

According to Noyes,

$$f(t)_{\mathrm{N}} = mt^{-3/2}\exp[-\pi m^2/(p^2 t)], \tag{20}$$

where $p = \int_0^\infty f(t)_{\mathrm{N}}\mathrm{d}t$ is the probability of the fact that particles undergo at least one reencounter; $(1 - p)$ is the probability of the fact that they never encounter again. Expressions for p and m have the forms:[17]

$$p = 1 - [1/2 + 3R/(2l)]^{-1}, \tag{21}$$

$$m \approx 1.036(1 - p)^2(R/l)^2\nu^{1/2}, \tag{22}$$

where R, l, and ν denote the same as in the previous equations. The diffusional shift l is a characteristic value in the relationship:

$$\Phi(s) = (1/l)\exp(-s/l), \tag{23}$$

where $\Phi(s)$ is the probability of shifting the particle by the distance s.[18]

The $k(t)$ constant in Eq. (15) can be found using the Noyes function (Eq. (20)). However, the testing parameters k_0 and k_∞ turn out to be incompatible with the same values in the similar Eq. (15).[15] Nevertheless, the Noyes function (see Eq. (20)) in the ingenious form is widely used for describing the molecular dynamics in liquids. At $t \gg m^2/p^2$ ($t \geq 10^{-12}$—10^{-11} s) $f(t) \approx mt^{-3/2}$ and does not coincide with Eq. (18).

The third, independent way for calculating $f(t)$ developed by Marshak[19] is the method of spherical harmonics, which is based on the stationary Boltzmann equation and is used for calculating the capture of neutrons by nuclei. We will not discuss this way and only note that the $f(t)$ function derived does not differ from that obtained by the diffusion equation and presented above (see Eqs. (13) and (17)).

Thus, there are two different functions, $f(t)_{\mathrm{N}}$ and $f(t)_{\mathrm{DE}}$ that need experimental testing.

Generalized dynamics of a radical pair

The probability of molecule formation from the triplet RP is determined by the integral of the product of functions of all three dynamics, molecular, spin, and chemical dynamics (see Eq. (2)). Then the calculation of integral (2) with the $f(t)_{\mathrm{N}}$ and $f(t)_{\mathrm{DE}}$ functions results in the expressions for probabilities of recombination P. Then numerical values of P and P^* with frequencies ω and ω^* of triplet-singlet transitions for nonmagnetic and magnetic RP should be found. Substituting P and P^* into Eq. (4), we obtain dependences of the coefficient of isotope separation α_{G} on the diffusion coefficient D. Just these dependences $\alpha_{\mathrm{G}}(D)$, and more exactly, $\alpha_{\mathrm{G}}(\log D)$, will be the test for the $f(t)$ function.

Substituting $f(t)_{\mathrm{N}}$ from Eq. (20) into Eq. (2) and calculating the integral, we obtain

$$P = \frac{\varepsilon p}{2m^2}\left\{\exp\left[-\frac{2m(\pi k)^{1/2}}{p}\right] - \right.$$
$$\left. - \exp\left\{-\frac{m(2\pi)^{1/2}}{p}\left[\left(k^2 + 4\omega^2\right)^{1/2} + k\right]^{1/2}\right\} \times \right.$$
$$\left. \times \cos\left\{\frac{m(2\pi)^{1/2}}{p}\left[\left(k^2 + 4\omega^2\right)^{1/2} - k\right]^{1/2}\right\}\right\}. \tag{24}$$

This expression gives the probability of molecule formation from the triplet RP *via* one of three channels of triplet-singlet conversion. All three channels ($T_{\pm,0} - S$) are approximately equivalent in zero magnetic field, and, hence, the total probability calculated by Eq. (24) should be tripled.

Integral (2) with the $f(t)_{DE}$ function from Eq. (17) has previously been calculated[20] and has the form

$$P = \frac{\varepsilon bR}{2r_0 BD}\left\{\frac{\exp(-2\mu\kappa)}{1+\kappa} + \exp(-2\mu u)\frac{(1-u)^2+v^2}{(1-u^2-v^2)+4v^2}\times\right.$$

$$\left.\times\,[v\sin(2\mu v)-(1+u)\cos(2\mu v)]\right\}, \tag{25}$$

where $\varphi = (1/B)\cdot(\omega/D)^{1/2}$; $\mu = B(r_0 - R)/2$; $\kappa = (1/B)\cdot(k/D)^{1/2}$;

$$v = \left[\frac{(\kappa^4+4\varphi^4)^{1/2}-\kappa^2}{2}\right]^{1/2};$$

$$u = \left[\frac{(\kappa^4+4\varphi^4)^{1/2}+\kappa^2}{2}\right]^{1/2}.$$

It is evident that at $\varepsilon = 0$ (the completely reflecting "white" sphere) $P = 0$. It is also evident that at $\varepsilon = 1$ (the "black," *i.e.*, the completely absorbing sphere of radius R) the P value in Eqs. (24) and (25) determines the probability P_1 of the first encounter of radicals after they parted at $t = 0$. (It should be noted that this encounter turned out to be the last one, because $\varepsilon = 1$.) However, at $0 < \varepsilon < 1$ the sphere is partially absorbing and then, analyzing the sequence of events in the RP, it is easy to show that probabilities of returns obey a descending geometric progression, and the total probability P_Σ is equal to the sum of terms of this infinite progression:

$$P_\Sigma = P_1 + P_1(p_0 - P_1) + P_1(p_0 - P_1)^2 + \ldots \tag{26}$$

or

$$P_\Sigma = \frac{P_1}{1 - p_0 + P_1}, \tag{27}$$

where

$$P_1 = \int_0^\infty f(t)\sin^2(\omega t)\exp(-kt)\mathrm{d}t, \tag{28}$$

$$p_0 = \int_0^\infty f(t)\exp(-kt)\mathrm{d}t. \tag{29}$$

According to the physical sense, p_0 is the probability of any return (independently of the spin state of the RP) and P_1 is the probability of return for a singlet state.

Now one can calculate probabilities P_1 and P_Σ with functions $f(t)_N$ and $f(t)_{DE}$ using Eqs. (24), (25), and (27).

Quantitative results

The following parameters were used in the numerical calculations of P_1 and P_Σ with the $f(t)_N$ and $f(t)_{DE}$ functions: $R = 5$ Å, $l = 5$ Å, $r_0 - R = \Delta = 0.1$ Å, $\varepsilon = 0.8$, $\nu = (6D/l^2)$. They are chosen rather arbitrarily, which, as we can see below, is not too important for drawing unambiguous results.

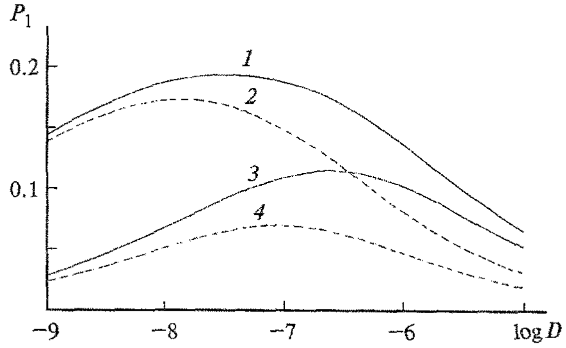

Fig. 2. Dependences of the probability P_1 calculated with the $f(t)_{DE}$ function on log$D$ at $k = 10^6$ s^{-1} (curves *1, 2*) and $k = 10^8$ s^{-1} (curves *3, 4*): *1* and *3,* for magnetic RP, $\omega^* = 22.2\cdot10^8$ rad s^{-1}; *2, 4,* for nonmagnetic RP, $\omega = 4.4\cdot10^8$ rad s^{-1}.

The P_1 and P_1^* values (for nonmagnetic and magnetic RP with ω and ω^* parameters, respectively) and the P_Σ and P_Σ^* values for the same RP allow one to calculate easily coefficients of one-stage isotope separation α and α_Σ by Eq. (4). The first of these coefficients determines the isotope separation for one (first) reencounter, and the second coefficient takes into account all multiple reencounters. The following values are accepted: $\omega = 4.4\cdot10^8$ rad s^{-1} and $\omega^* = 22.2\cdot10^9$ rad s^{-1}, which approximately correspond to the rate of triplet-singlet conversion in the RP ($PhCH_2^{\cdot}$ $^{\cdot 12}COCH_2Ph$) and ($PhCH_2^{\cdot}$ $^{\cdot 13}COCH_2Ph$) generated by photolysis of dibenzylketone.

Examples of the results of calculations are shown in Fig. 2, in which the dependences of P_1 on log$D$ calculated by Eq. (25) with the $f(t)_{DE}$ function are presented. It can be seen that $P_1^* > P_1$ always (at any values of log$D$); however, there is a region of log$D$ in which differences in them are maximum and the P_1^*/P_1 ratio reaches 1.6 to 1.8. It is evident that α values are also maximum at these values of log$D$.

The dependences of α and α_Σ on log$D$ calculated by Eqs. (24), (25), (27), and (4) with the $f(t)_{DE}$ and $f(t)_N$ functions are shown in Fig. 3. Two important conclusions follow from these results. First, it is evident that contributions of reencounters to the isotope separation are comparable in value with the contribution of the first encounter, although their probabilities decrease according to the geometric progression. However, the decrease in the probability of reencounters is excessively compensated by the completeness of triplet-singlet conversion and the increase in the efficiency of isotope selection for each next encounter.

Second, both dependences α(log$D$) and α_Σ(log$D$) pass through maxima; however, position of maxima and the shapes of the curves differ for the $f(t)_N$ and $f(t)_{DE}$

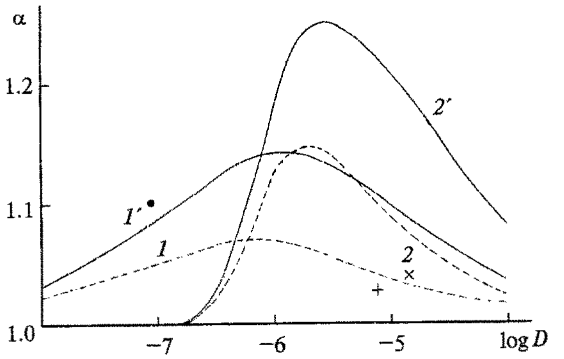

Fig. 3. Dependences of α (curves *1, 2*) and α_Σ (curves *1′, 2′*) on log*D* calculated with the $f(t)_{DE}$ (*1, 1′*) and $f(t)_N$ functions (*2, 2′*). Experimental α values are indicated by points: in benzene (+), hexane (×), and cyclohexanol (•).

functions. With the Noyes function, the maximum is shifted to the region of fast diffusion, and the α(log*D*) and α_Σ(log*D*) dependences descend sharply in the region of slow diffusion to reach unity even at $D > 10^{-7}$ cm^2 s^{-1}. With the $f(t)_{DE}$ function, the α(log*D*) and α_Σ(log*D*) are smoother and stretched far to the region of slow diffusion up to $D \approx 10^{-9}$ cm^2 s^{-1} (see Fig. 3).

At the final stage, the theoretical α(log*D*) and α_Σ(log*D*) dependences presented in Fig. 3 should be compared to experimental dependences. First, points in Fig. 3 indicate experimental values of α in hexane, benzene, and cyclohexanol measured by the isotope enrichment in dibenzylketone in these solvents during its photolysis.[21,22] The α values in benzene and hexane are lower than calculated values, but this fact is not indicative, because absolute calculated α values are sensitive to parameters, which were chosen somewhat arbitrarily (see above). The fact that the α value in cyclohexanol is high even in the range of $D < 10^{-7}$ cm^2 s^{-1}, where the Noyes function predicts complete absence of isotope separation (α = 1), is much more convincing. It is clear that the $f(t)_{DE}$ function corresponds better to the experimental data.

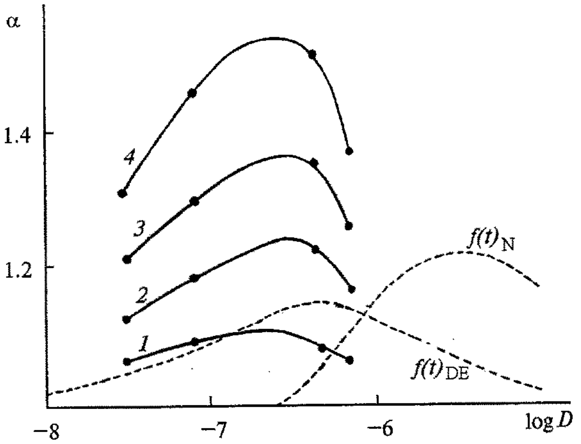

Fig. 4. Experimental dependences of α on log*D* during photolysis of various isotopic forms of dibenzylketone: *1*, $Ph^{13}CH_2COCH_2Ph$; *2*, $PhCH_2{}^{13}COCH_2Ph$; *3*, $Ph^{13}CH_2{}^{13}COCH_2Ph$; *4*, $Ph^{13}CH_2{}^{13}CO^{13}CH_2Ph$ (see Ref. 23). Theoretical curves calculated with the $f(t)_N$ and $f(t)_{DE}$ functions are shown by dotted lines.

Second, the experimental α(log*D*) dependences during photolysis of various isotope forms of dibenzylketone in glycerol—*tert*-butyl alcohol mixtures are shown in Fig. 4. The theoretical α_Σ(log*D*) dependences from Fig. 3 with the $f(t)_{DE}$ and $f(t)_N$ functions are shown by dotted lines. Although there is no quantitative agreement (see below), it is clear that the positions and the shapes of the experimental curves correspond significantly better to the $f(t)_{DE}$ function and are not described by the $f(t)_N$ function at all.

Now let us discuss the quantitative difference in theoretical and experimental values of α. Theoretical α values are calculated per act of regeneration of a molecule from the RP. Under this condition, the averaged content of an isotope (δ) in regenerated molecules relative to its content in initial molecules (δ_0) is determined by the relationship:

$$\delta = (P_\Sigma{}^*/P_\Sigma)\delta_0. \qquad (30)$$

However, when a regenerated molecule undergoes multiple repeated decomposition acts followed by regeneration acts, the isotope enrichment obeys the equation

$$S = \delta/\delta_0 = (P_\Sigma{}^*/P_\Sigma)^n, \qquad (31)$$

where *n* is the number of decomposition—regeneration cycles.

Since $P_\Sigma{}^* > P_\Sigma$, the multicascade character of the process (high *n*) provides considerable isotope enrichment, which is confirmed experimentally. Moreover, *n*, the degree of the cascade character of the process, can be evaluated by comparing the experiment and the theory.

In addition, Eqs. (24) and (25) predict that the coefficient of isotope separation α depends on the chemical dynamics of the RP, *i.e.*, on the rate constant *k*. An example of the dependences α(log*D*) calculated with the $f(t)_{DE}$ function by Eq. (25) at various *k* values is presented in Fig. 5. It is clear that α values decrease as *k* increase, *i.e.*, the isotope selectivity decreases considerably when the chemical dynamics restricts the lifetime of the RP and the completeness of its spin conversion. The effect of spin dynamics is the most pronounced at $k > \omega, \omega^*$.

Finally, the problem of the effect of initial separation of partners in the RP ($\Delta = r_0 - R$) on the generation of reencounters and repeated selection is of interest. The theoretical dependences α(log*D*) at various Δ values are presented in Fig. 6. It follows from analysis of these dependences that an increase in Δ results in a decrease in the probability of reencounters (that is reasonable) and in a decrease in the α coefficient. Curves *1* and *2*

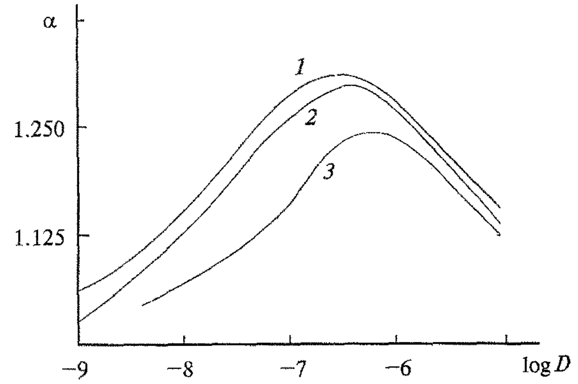

Fig. 5. Dependences of α on log*D* at k/s^{-1} = 0 (*1*), 10^6 (*2*), and 10^8 (*3*) calculated with the $f(t)_{DE}$ function according to Eq. (25).

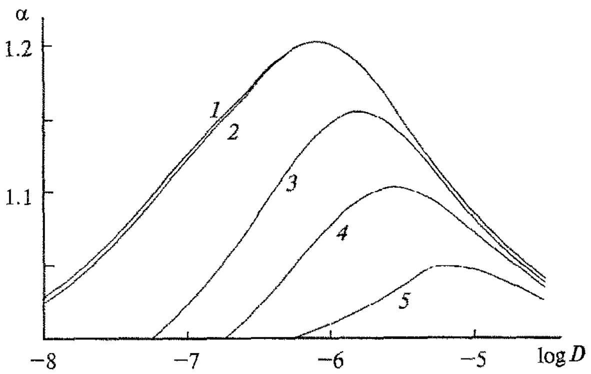

Fig. 6. Theoretical dependences of α on log*D* at various initial distances between partners of the RP: Δ/Å = 0 (*1*), 0.1 (*2*), 2 (*3*), 4 (*4*), and 9 (*5*). Calculation for $k = 2 \cdot 10^7$ s^{-1}, $\omega = 4.4 \cdot 10^8$ rad s^{-1}, $\omega^* = 22.2 \cdot 10^8$ rad s^{-1}.

corresponding to Δ = 0 and Δ = 0.1 Å are worthy of special attention. These curves almost coincide, and this important fact means that breaks of gradients of diffusional flows and violation of the Fick law on the surface of the reaction sphere (see above) are insignificant from the quantitative viewpoint. However, this does not remove requirements for physically rigorous formulation of the diffusion problem.

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