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Cascade Strategy of the Chemically Induced Magnetic Isotope Fractionation

Anatoly L. Buchachenko and Vitaly L. Berdinsky*

Institute of Chemical Physics, 142432 Chernogolovka, Moscow Region, Russia

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A cascade theory of isotope fractionation in partly reversible reactions involving triplet radical pairs is developed. Each step of the cascade process is accompanied by nuclear spin selective renaissance of the molecule after its dissociation and results in accumulation of magnetic isotopes in the regenerated molecule. The factors stimulating nuclear spin selectivity in the cascase process are considered. The size of the microreactor and microwave pumping of the radical pairs are shown to be of paramount importance to provide a highly efficient chemically induced magnetic isotope fractionation.

Introduction

Among many remarkable phenomena discovered in spin chemistry, the magnetic isotope effect (MIE) seems to be the most outstanding. It arises in *electron spin selective* chemical reactions, which appear to be inevitably *nuclear spin selective* if electron and nuclear spin systems are coupled by Fermi or hyperfine interactions (HFI). Then the nuclear spin selectivity results in differentiation of the reaction rates relative to the *nuclear spin* and *nuclear magnetic momentum* of the reagents.[1] In contrast to the classical isotope effect, which sorts isotopic nuclei with respect to their mass, MIE selects the nuclei according to their spin and magnetic momentum. This is a fundamental distinction between these two isotopic effects.

The detailed comparative analysis of both isotope effects has been given recently.[1a] It was demonstrated that the fundamental problems of the chemical physics of MIE are now well understood and that the theoretical limit of the nuclear spin selectivity is clearly formulated. The most important and intriguing problem that remains to be solved is how to reach this theoretical limit.

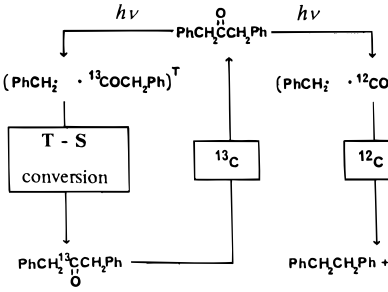
The purpose of this paper is to develop new insight into the kinetics of spin-selective reactions, which reveals new resources to stimulate MIE-induced isotope fractionation.

Kinetics versus Statistics. MIE-induced sorting of isotope nuclei may be illustrated by photolysis of dibenzyl ketone (DBK), which is known to occur via an excited triplet state and a triplet radical pair stage (Scheme 1).

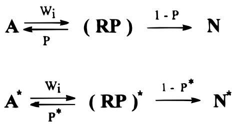
The pair either undergoes the HFI-induced triplet−singlet spin conversion and recombines, regenerating the starting DBK molecule, or dissociates into the separated radicals $PhCH_2$ and $PhCH_2CO$; the latter splits into $PhCH_2$ and CO. Dibenzyl $(PhCH_2)_2$ and carbon monoxide are practically the only reaction products.

Since the rate of triplet−singlet conversion of the pairs with ^{13}C is much faster than that of the pairs with ^{12}C, the former predominantly recombine; the latter mostly dissociate, generating dibenzyl and carbon monoxide. As a result, regenerated DBK molecules accumulate magnetic ^{13}C nuclei, whereas carbon monoxide collects nonmagnetic ^{12}C nuclei. Ultimately, DBK decomposes but its decomposition products are enriched with ^{13}C nuclei. Thus, RP is a spin-selective chemical reactor sorting magnetic and nonmagnetic isotopes.

SCHEME 1: Isotopic Sorting in the Photolysis of Dibenzyl Ketone Molecules



SCHEME 2: Kinetic Presentation of Partly Reversible Reactions



The kinetic scheme of this as well as of many similar partly reversible reactions (Scheme 2) implies the generation of RP, which is able either to recombine (with a probability P) or to produce reaction product N (with a probability $1 - P$).

The same is valid for the molecule A* differing from A only by substitution of one of the carbon ^{12}C nuclei with a magnetic ^{13}C nucleus and, consequently, by the recombination probability P^* of the corresponding RP*. Note that in Scheme 2 the rate w_i of RP generation is supposed to be identical for both isotopic molecules A and A*; i.e., we ignore a classical mass-dependent isotope effect, which is known to be negligibly small in comparison with MIE.[1a]

For the chemically reacting system in which both isotopic forms A and A* are presented, the following characteristic parameters are introduced. $\delta = [A^*]_0/[A]$ is the content of asterisked isotope (^{13}C, in particular) during the reaction. δ_0 is the initial value of δ at $t = 0$. $F = ([A]_0 - [A])/[A]_0$ is a chemical conversion of A molecules. $F = ([A^*]_0 - [A^*])/[A^*]_0$ is a chemical conversion of A* molecules. Now there is no problem deriving the following equations relating isotope enrichment $S = \delta/\delta_0$ to the chemical conversion F or F^* (for details see ref 1d):

$$S = (1 - F)^{\alpha};\quad \alpha = (P - P^*)/(1 - P) \tag{1}$$

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$$S = (1 - F^*)^{\alpha^*}; \quad \alpha^* = (P - P^*)/(1 - P^*) \qquad (2)$$

Scheme 2 results in the equations describing the kinetics of chemical decomposition of A and A* molecules:

$$-\mathrm{d[A]/d}t = w_i[\mathrm{A}](1 - P) \qquad (3)$$

$$-\mathrm{d[A^*]}\ /dt = w_i[\mathrm{A^*}](1 - P^*) \qquad (4)$$

The reduced ratio of the decay rates for A and A* molecules defines the one-step enrichment coefficient α_G, which characterizes the efficiency of MIE-induced isotope separation:

$$\left[\frac{\mathrm{d[A]/d}t}{w_i[\mathrm{A}]}\right]\left[\frac{\mathrm{d[A^*]/d}t}{w_i[\mathrm{A^*}]}\right]^{-1} = \frac{1 - P}{1 - P^*} = \alpha_G \qquad (5)$$

Combining eqs 1, 2, and 5, one can obtain the following important relations:

$$\alpha_G = \frac{\ln(1 - F)}{\ln(1 - F^*)} \qquad (6)$$

$$\alpha_G = \frac{1 - P}{1 - P^*} \qquad (7)$$

$$S = \frac{1 - F^*}{1 - F} \qquad (8)$$

They express the kinetic parameters of MIE, α_G, and S in terms of the RP recombination probability and chemical conversion.

Now we address the statistic behavior of an individual molecule subjected to chemical reaction. Suppose, molecule A (DBK, for instance) decomposes the first time, generating RP as shown in Scheme 1. The probability of the RP recombination and, therefore, regeneration of the molecule A is indeed the probability P for the molecule to survive. Further, this renewed molecule has a chance to experience a second dissociation into the RP, which is again able to recombine and regenerate the starting molecule. The probability for the molecule A to survive after the second cycle of decomposition–regeneration is P^2. In this way, one can derive that if the molecule A suffers a cascade of n reactive cycles of decomposition–regeneration, the final probability for the molecule to survive is P^n. Figure 1 illustrates schematically one cycle of the cascade.

According to the ergodicity hypothesis, the survival probability P^n is equivalent to the fraction of the remaining molecules A if their chemical conversion F is achieved. Then it follows that

$$P^n = 1 - F \qquad (9)$$

and similarly, for the A* molecules

$$(P^*)^{n^*} = 1 - F^* \qquad (10)$$

Combining eqs 6–8 with eqs 9 and 10, one can obtain new relations between isotope enrichment and cascade parameters n and n^*:

$$S = (P^*)^{n^*}/P^n \qquad (11)$$

$$\alpha_G = \frac{n \ln P}{n^* \ln P^*} \qquad (12)$$

Finally, it follows from eqs 7 and 12 that the cascade parameters n and n^* are definitely related to the recombination, the renaissance probabilities P and P^*:

$$\frac{n^*}{n} = \left(\frac{\ln P}{1 - P}\right)\Big/\left(\frac{\ln P^*}{1 - P^*}\right) \qquad (13)$$

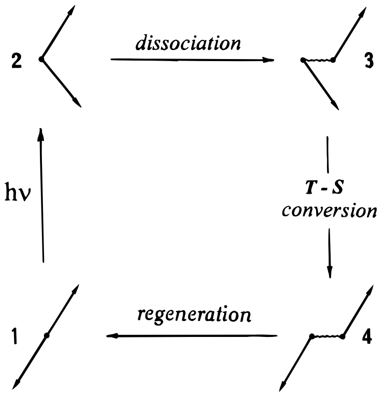

Figure 1. Four-step spin-selective cascade of the photoinduced dissociation–regeneration process. The starting molecule **1** excited in triplet state **2** dissociates to triplet radical pair **3**. Spin transformation converts the pair into the singlet RP **4**, regenerating the starting molecule **1**.

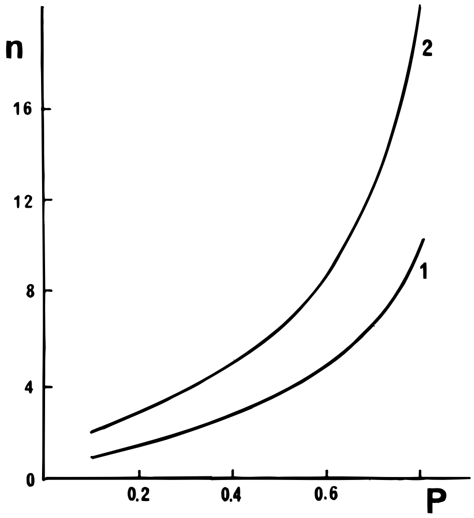

Figure 2. Cascade parameter n as a function of the recombination probability P at the fixed conversion $F = 0.9$ (1) and 0.99 (2).

Collection of these equations allows us to formulate a strategy of stimulation MIE-induced isotope sorting in chemical reactions.

Cascade Strategy. The key requirement of this strategy is to maintain a high cascade efficiency of chemical reactions. Each regeneration, each renaissance of the reacting molecule is a nuclear spin selective event resulting in highly efficient total isotope fractionation.

The absolute magnitudes of cascade parameters n and n^* are directly related to the chemical conversion as eqs 9 and 10 predict. At fixed conversion, the cascade parameter n is a function of the recombination probability as illustrated in Figure 2. The general conclusion is that an increase in both F and P results in enhancement of the efficiency of the cascade process independently of the isotopic molecules it concerns. As long as P^* is greater than P, then n^* is greater than n for the identical conversions F and F^*; i.e., the higher recombination probability of the RPs with magnetic nuclei promotes the more efficient cascade process for the RP precursor, the molecule with magnetic nuclei.

TABLE 1: Recombination Probabilities *P*, One-Step Enrichment Coefficients α_G, and Ratios of the Cascade Parameters *n/*n***

precursor molecule	radical pair		*P*	α_G	*n**/*n*
DBK[a]	$PhCH_2$	$COCH_2Ph$	0.52		
	$Ph^{13}CH_2$	$COCH_2Ph$	0.57	1.05	1.04 [d]
	$Ph^{13}CH_2$	$CO^{13}CH_2Ph$	0.60	1.12	1.07[d]
$Ph^{13}CH_2$	$^{13}COCH_2Ph$		0.67	1.40	1.12[d]
	$Ph^{13}CH_2$	$^{13}CO^{13}CH_2Ph$	0.70	1.52	1.15[d]
MDB[b]	PhCO	$CH(CH_3)Ph$	0.55		
	PhO	$CH(CH_3)Ph$	0.59	1.09	1.03[d]
DPP[c]	$PhCH(CH_4)CO$	$CH(CH_3)Ph$	0.166		
	$PhCH(CH_3)^{13}CO$	$CH(CH_4)Ph$	0.215	1.06	1.10[d]

[a] Dibenzyl ketone; photolysis in hexadecyltrimethylammonium bromide.[1d,3] [b] Methyldeoxybenzoin; photolysis in sodium dodecyl sulfate micelles.[4] [c] Diphenylpentanone; photolysis in sodium dodecyl sulfate micelles.[5] [d] With respect to the corresponding $^{12}C-RP$.

The ratio of cascade parameters *n**/*n*, as well as the one-step enrichment coefficient, characterizes isotope selection regardless of the chemical conversion and depends on *P* and *P** only. Now we will analyze the factors controlling the cascade process and stimulating the MIE-induced isotope fractionation.

Space-Restricted Diffusion. The most powerful way to increase recombination probability and, therefore, the cascade parameters is to localize a reaction in a microreactor of confined geometry, such as micelles, zeolite, porous glass cavities, etc. A radical pair imprisoned in such a trap is forced to recombine so that the RP precursor molecule is predestinated to participate in a multicascade spin-selective process. For instance, the recombination probability of the triplet RP consisting of benzoyl and *sec*-phenethyl radicals, regenerated by the photolysis of methyldeoxybenzoin in benzene, was shown to be negligibly small, no more than 0.01.[2] However, for the same RP locked in sodium dodecyl sulfate, the micelle recombination probability is more than 50 times higher.

Table 1 clearly demonstrates the large magnitudes of these probabilities for the triplet radical pairs generated by photolysis of ketones in micelles. The one-step enrichment coefficients and the ratios of the cascade parameters collected in the table follow these probabilities, as seen, in particular, from the sequence of isotopic RPs generated from DBK.

The forced recombination is a necessary but not sufficient factor to guarantee efficient isotope selection. Another factor, a ratio *P**/*P*, which differentiates cascade parameters *n** and *n*, is controlled by the competition of spin and molecular dynamics of the radical pair in the microreactor. If spin dynamics is slow and limits the rate of the RP recombination, the difference in *P** and *P* is large and follows the difference in hyperfine coupling energy of the recombining RPs. However, if spin dynamics is fast, the recombination is controlled by diffusional reencounters of the RP partners in the microreactor. In this case, magnetically different RPs substantially lose their magnetic identity so that the probabilities *P** and *P* tend toward equalizing.

A quantitative criterion of these two dynamic regimes is the $\tau_{TS} - \tau_{reen}$ relation, where τ_{TS} is the characteristic time of the RP triplet−singlet spin conversion and τ_{reen} is the time interval between diffusional reencounters. The condition $\tau_{TS} \gg \tau_{reen}$ identifies a regime when the spin transformation is a rate-limiting process. The inverted relation, $\tau_{TS} \ll \tau_{reen}$, specifies a regime of diffusional reencounters as the rate-limiting events.

A critical factor controlling the competition of these two dynamic regimes is the size of the microreactor in which RP is embedded. Using pure geometrical reasoning, one can derive a simple relation[6]

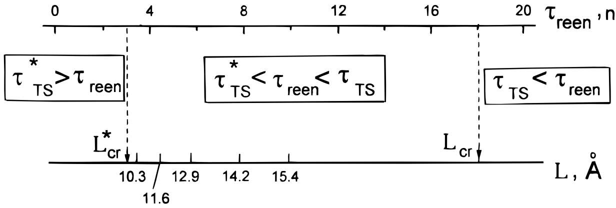

Figure 3. relation between two scales characterizing the time interval τ_{reen} between reencounters of the RP partners and the size *L* of the microreactor. L_{cr} and L_{cr}* label the critical sizes of microreactors in which the boundary conditions $\tau_{reen} = \tau_{TS}$ and $\tau_{reen} = \tau_{TS}^*$ are satisfied respectively for the nonmagnetic and magnetic RPs. These conditions correspond to the border between the reencounter and spin dynamic regimes of the RP recombination. Figures on the scale *L* denote the radii of micelles made from the sodium salts of octyl, nonyl, decyl, undecyl, and dodecyl sulfate.[4,5]

$$L^3 = 3RD\tau_{reen} \tag{14}$$

where *L* is the radius of the spherical microreactor (for micelles, for instance, it is determined as the maximum length of an extended surfactant molecule), $R = r_1 + r_2$ is the distance of the closest approach of the radical partners (with radii r_1 and r_2, respectively) in contact pair, and *D* is the total diffusion coefficient of the partners in microreactor, $D = D_1 + D_2$.

A synchronism of spin and diffusional dynamics, which implies coincidence in time of two events, triplet−singlet spin transformation of the RP and diffusional reencounter of the RP partners (then the equation $\tau_{TS} = \tau_{reen}$ holds), ensures the best nuclear spin selectivity. Using eq 14, one can evaluate the critical size of the microreactor that satisfies the synchronism, that is, the equality $\tau_{TS} = \tau_{reen}$. For the typical nonmagnetic RP, such as RP generated by photolysis of $^{12}C-DBK$, $\tau_{TS} = 16$ ns. Substituting it in eq 14 instead of τ_{reen} and assuming $D = 2 \times 10$ cm/s, $R = 6$ Å, typical values for the RP in micelles, one can estimate $L_{cr} = 18$. This critical radius corresponds to the boundary between two kinetic regimes: at $L \ll L_{cr}$, the rate-limiting process is spin transformation so that $\tau_{TS} > \tau_{reen}$, and at $L > L_{cr}$ a bottleneck of the recombination process is the diffusional reencounters (we will define it as a reencouner regime $\tau_{TS} < \tau_{reen}$).

For the magnetic RP generated by the photolysis of $^{13}C-DBK$, $\tau_{TS}^* = 3$ ns. Substituting this magnitude in eq 14 instead of τ_{reen} and using the parameters *D* and *R* identical with those for the nonmagnetic RP, one can evaluate $L_{cr}^* = 10$ Å. Again, L_{cr}* characterizes the critical size of the microreactor: at $L < L_{cr}^*$ the rate of recombination of magnetic RP is limited by spin dynamics ($\tau_{TS} > \tau_{reen}$), and at $L > L_{cr}^*$ diffusional reencounters control the rate of the recombination process (the reencounter regime, $\tau_{TS} < \tau_{reen}$).

These considerations are summarized in Figure 3, which shows two scales, *L* and τ_{reen}, interrelated by eq 14. The magnitudes of critical radii L_{cr}* and L_{cr} for the microreactors with embedded magnetic and nonmagnetic RPs are indicated by arrows as well as relations between τ_{TS} and τ_{reen} characterizing dynamic regimes of recombination. The remarkable feature is the size of experimentally studied micelles as the microreactors falls into the range from 10 to 18 (it corresponds to the time domain of τ_{reen} from 3 to 16 ns), in which *the recombination of magnetic RP occurs in the reencounter regime, but the recombination of nonmagnetic RP is controlled by spin dynamics.* It is also clear that for the microreactors with $L > L_{cr}$ (to the right from L_{cr} in Figure 3), the recombination of both magnetic and nonmagnetic RPs occurs in the reencounter

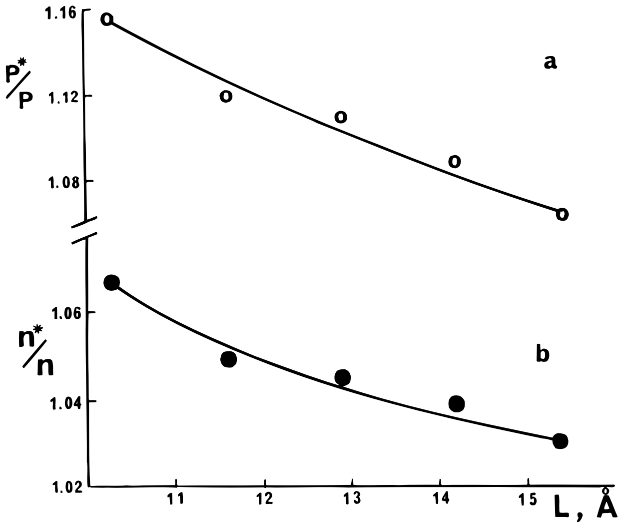

Figure 4. Ratios P^*/P (a) and n^*/n (b) as a function of the micelle size L. The values P and P^* are taken from res 4 and 5.

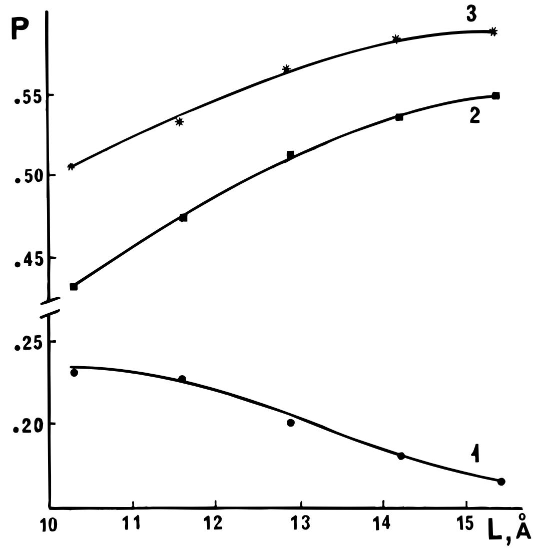

Figure 5. Recombination probabilities P as a function of the micelle size L for the ^{12}C−RP from the DPP molecule (curve 1), and for the ^{12}C−RP and ^{13}C−RP from the MDB molecule (curves 2 and 3, respectively).[4,5]

regime, whereas at $L < L_{cr}^*$ (to the left from L_{cr}^* in Figure 3) the recombination is governed by spin dynamics. The former, as shown above, is characterized by low nuclear spin selectivity and by low ratios of P^*/P; the latter ensures the most effective selectivity, as large as HFI is able to produce.

Now we are faced with two trends. On one hand, traveling along the scale of L from the right to the left results in shifting the recombination kinetics from the reencounter regime to the spin dynamic regime so that an increase in the selectivity parameter P^*/P is expected as the microreactor size decreases. In accordance with this prediction Figure 4 demonstrates that for the RPs from MDB photolysis in micelles of a varying size, the contraction of the microreactor stimulates the growth of the ratio P^*/P as well as the cascade ratio n^*/n.

On the other hand, the contraction of the microreactor decreases τ_{reen} and therefore increases the absolute magnitudes of P, P^*, n, and n^*. Figure 5 illustrates this dependence for the short-living RP (the lifetime is about 22 ns[7] due to fast decarbonylation of acyl radical) generated by photolysis of DPP (see Table 1). The growth of P in small micelles is also in a qualitative agreement with the increase of the rate constants of geminate recombination of the RPs in cationic and anionic micelles.[8]

Both trends, the enhancement of the selectivity parameters P^*/P (and n^*/n) and the growth of parameters P^* and P themselves, are *in favor of a small microreactor as a nuclear spin selective device.* However, this general conclusion is violated if spin-nonselective processes, competing with spin-selective recombination, become important. For instance, the recombination probabilities P and P^* for the RPs generated by photolysis of MDB (see Table 1) decrease as the size of micelles decreases (Figure 5, curves 2 and 3), contrary to the theoretical predictions and experimental results for the short-living RPs from DPP (Figure 5, curve 1). The reason for the discrepancy is that for the long-living RP from MDB ($\tau_{life} \gg \tau_{reen}, \tau_{TS}, \tau_{TS}^*$), an escape of radical partners outside the micelle becomes noticeable. The rate of escape increases as the microreactor size decreases. It follows from the simplest geometrical arguments[9] and is supported by experimental findings.[8] This leakage of radicals from micelles results in a general decrease in the recombination probabilities as shown in Figure 5, curves 2 and 3. Nevertheless, despite the fact that the absolute magnitudes of P and P^* for the RPs from MDB decrease in small micelles, the ratios P^*/P and n^*/n characterizing nuclear spin selectivity remain the dominating factors (Figure 4) so that ultimately they compensate and even exceed the loss of regeneration efficiency in small microreactors.

The preference of small microreactors to enhance chemically induced magnetic isotope fractionation as a general tendency is faced with a restriction imposed by exchange interaction. In small microreactors, a short-range exchange interaction retards spin transformation of the RPs and supresses the RP recombination. If a microreactor is not too small, the exchange interaction is not too large and supresses spin conversion of the nonmagnetic RPs more strongly than that of the magnetic RPs owing to the difference in the HFI energy of these pairs. The exchange interaction acts most effectively between L_{cr}^* and L_{cr}, when recombination of magnetic pairs occurs in the reencounter regime (and therefore is weakly subjected to exchange interaction), but recombination of nonmagnetic RPs is controlled by spin dynamics and strongly suppressed by the exchange interaction. It results in the growth in the P^*/P and n^*/n ratios and increases the isotope selectivity.

However, in very small micelles (at $L < L_{cr}^*$), when the exchange interaction prevails over HFI, it strongly suppresses spin conversion of both magnetic and nonmagnetic RPs and is expected to decrease dramatically both P and P^* as well as cascade parameters n and n^*. Then the competing spin-nonselective channels (escape, for instance) become important and destroy the total nuclear spin selectivity. The influence of the exchange interaction on the spin dynamics in microreactors was quantitatively studied in a series of excellent papers by Tarasov, Turro, et al.[4,5,10]

Spin Catalysis. Recombination of the triplet RP is strongly stimulated by the presence of a third spin carrier, a radical, or paramagnetic ion. The exchange interaction of this spin carrier with the RP partners accelerates triplet−singlet conversion of the pair and increases the recombination probability so that the third spin acts as a recombination spin catalyst.[11]

At first sight, spin catalysis is a promising and powerful tool to enhance the regeneration of the RP precursor molecule and the efficiency of the cascade process. Intuitively, it is evident that the spin catalysis should increase the absolute magnitudes of P and P^*; however, it is also clear that spin catalysis is not sensitive to the nuclear spin of the RP (at least, at first approximation, which implies ignoring the HFI in the three-spin system[11]). Thus, spin catalysis equally influences the spin dynamics of magnetic and nonmagnetic RPs and does not differentiate P and P^*. The total result may be derived only by quantitative analysis of the spin catalytic contribution into the total recombination probability.

The recombination probabilities P and P^* may be expressed in terms of the rate constants:

$$P = k_r/(k_r + k_{esc})$$

$$P^* = k_r^*/(k_r^* + k_{esc}) \qquad (15)$$

where k_r and k_r^* are the regeneration rate constants, k_{esc} is the total rate constant of all other processes in the RP (dissociation, disproportionation, transformation), which are supposed to be spin-nonselective. The probabilities of spin-catalyzed recombination P_{sc} and P_{sc}^* may be described similarly:

$$P_{sc} = (k_r + k_{sc})/(k_r + k_{esc} + k_{sc})$$

$$P_{sc}^* = (k_r^* + k_{sc})/(k_r^* + k_{esc} + k_{sc}) \qquad (16)$$

where k_{sc} is the rate constant of the spin catalytic recombination, which (as was mentioned above) is supposed to be nonsensitive to the nuclear spin of the RP.

Now, substituting eqs 15 and 16 in eq 7, one can derive the ratio of one-step enrichment coefficients α_G^{sc} and α_G for the two regimes of recombination, catalytic and noncatalytic:

$$\alpha_G^{sc}/\alpha_G = [(k_r + k_{esc})/(k_r + k_{esc} + k_{sc})][1 + k_{sc}/(k_r^* + k_{esc})] \qquad (17)$$

The quantitative analysis of the equation reveals that at any reasonable magnitude of the rate constants, the ratio, i.e., spin catalysis, ultimately decreases the efficiency of MIE-induced isotope fractionation. Although spin catalysis stimulates RP recombination and increases the absolute values of P and P^*, the loss of nuclear spin selectivity along the spin catalytic channel remains the dominating factor that suppresses the total isotope selectivity of the recombination reaction.

Figure 3 provides an obvious physical understanding of this conclusion. In the experimentally feasible range of microreactors between L_{cr}^* and L_{cr}, the recombination of magnetic pairs occurs in the reencounter regime, and therefore, it is weakly subjected to spin catalytic promotion, since spin catalysis affects only the spin dynamics. However, the recombination of nonmagnetic pairs occurs in the spin dynamic regime so that it is strongly influenced by spin catalysis. Hence, spin catalysis accelerates the recombination of nonmagnetic pairs more efficiently than that of magnetic pairs. The final result is a loss of the nuclear spin selectivity to such an extent that it cannot be compensated by general growth in the regeneration of precursor molecules.

Microwave Pumping. A beautiful way to enhance the nuclear spin selectivity is microwave pumping of triplet RP. The idea of a microwave-induced magnetic isotope effect was formulated in 1981[12] and illustrated experimentally for the $^{13}C/^{12}C$ isotope pair in DBK photolysis[13] and for the H/D isotope pair in the photoreduction of anthraquinone in partly deuterated SDS micelles.[14]

The detailed theoretical study of the behavior of radical pairs under microwave pumping has been carried out by Salikhov and Molin.[15] A great variety of regimes of manipulation with RP spin states by microwaves can be combined into two groups: *spin inversion* to convert spin states between $T_\pm$ and T_0 with the following fast HFI-induced T_0−S transformation and *spin locking* to lock triplet states and retard or even prevent triplet−singlet conversion. In the first case, microwave pumping stimulates RP recombination; in the second case, it depresses RP spin conversion and recombination. The former is possible at $\gamma H_1 < a$, the latter is satisfied at $\gamma H_1 > a$, where H_1 is an amplitude of the microwave field, γ is the gyromagnetic ratio, and a is a hyperfine coupling constant.[15,16]

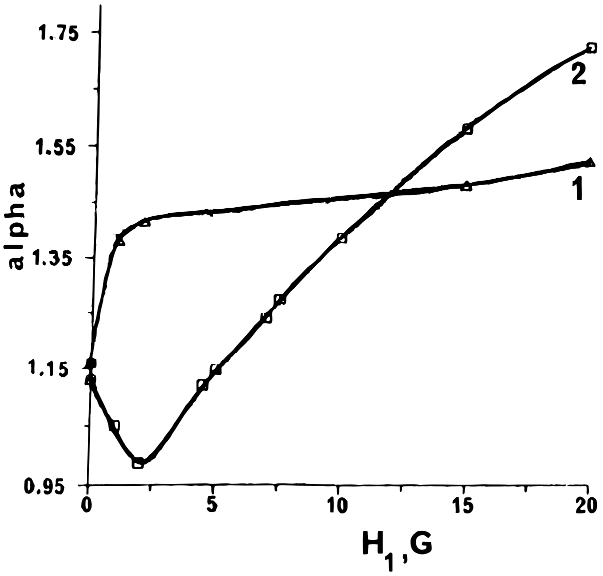

Figure 6. Calculated one-step enrichment coefficient α_G for the $^{13}C/^{12}C$ isotopic pair as a function of the microwave field H_1 at the microwave pumping of magnetic (curve 1) and nonmagnetic (curve 2) radical pairs of phenacyl and benzyl radicals, the precursor of the DBK molecule.[17]

Microwave pumping as a new tool to control RP recombination provides a new strategy to enhance nuclear spin selectivity of the RP reactions. The most promising would be a combination of two microwave actions: low-amplitude ($\gamma H_1 < a$) pumping of magnetic RPs, which stimulates triplet−singlet conversion and accelerates their recombination, and high-amplitude ($\gamma H_1 > a$) pumping of nonmagnetic RPs, which retards or even locks RP spin conversion, preventing their recombination. Under these conditions, the ratios P/P^* and n^*/n are expected to increase strongly.

This simultaneous and selective pumping of both isotopic sorts of RPs is feasible only if the ESR spectra of the pairs are not overlapped, that is, ESR transitions in these two sorts of pairs are not superimposed. It is reliable for the $^{13}C/^{12}C$ pairs, where $a(^{13}C)$ in the magnetic RPs is usually much larger than a(H) in nonmagnetic pairs so that ESR transitions in both pairs may be pumped simultaneously but selectively in frequencies.

However, the efficiency of the microwave pumping is different for the two sorts of RPs. As seen in Figure 3, the majority of the experimentally available microreactors are locked between L_{cr}^* and L_{cr}, where recombination of the magnetic RPs occurs in the reencounter regime, while that of the nonmagnetic RPs happens in the spin dynamic regime. It means that the low-amplitude stimulating pumping of magnetic RPs is much less effective than the high-amplitude suppressing pumping of the nonmagnetic RPs.

Figure 6 illustrates the behavior of one-step enrichment coefficients as a function of the microwave amplitude H_1. The pumping of magnetic RPs (curve 1) increases P^* and, according to eq 7, increases α_G. The pumping of nonmagnetic RPs (curve 2) at low H_1 increases P and results at first in decreasing. The minimum corresponds to the change in the pumping regime from *spin inversion* to *spin locking*. At high H_1 values, spin locking stops triplet−singlet conversion of nonmagnetic pairs and decreases P, resulting in the increase in α_G according to eq 7. Figure 6 clearly demonstrates that the contribution of spin locking in the microwave-stimulated isotope fractionation prevails over that of spin inversion. In accordance with this conclusion, the growth of α_G at the microwave pumping of the ^{13}C−RPs in DBK photolysis was shown to be rather low, 3−4% with respect to α_G without pumping, despite the high amplitude (about 6 G) of H_1.[13]

Conclusion

Cascade theory of partly reversible spin-selective chemical reactions developed in this paper discloses very clearly the factors stimulating the nuclear spin selectivity and controlling magnetic isotope fractionation. Cascade strategy based on this theory determines a hierarchy of the stimulating factors. Priority belongs to the size of microreactor, which, first, specifies an efficiency of the regeneration process and, second, regulates the kinetic regime of recombination. The size of the microreactor is a powerful factor that allows us to change deliberately the reencounter regime into the spin dynamic regime and vice versa. The cascade strategy forecasts an advantage of small microreactors as nuclear spin selective molecular devices. Moreover, in most experimental microreactors, the recombination of the magnetic radical pairs occurs in the reencounter regime but the recombination of nonmagnetic pairs is controlled by spin dynamics. It opens a delicate opportunity to manipulate with these pairs independently.

Among all factors stimulating the radical pair recombination and increasing cascade parameters, microwave pumping is the most promising. In contrast to spin catalysis, which stimulates the recombination of both magnetic and nonmagnetic RPs (but the domination of the latter contribution fails to increase the ratios P^*/P and n^*/n), microwave pumping is able to stimulate the recombination of magnetic pairs and to suppress that of nonmagnetic pairs simultaneously. Such a cooperative effect may result in an unlimited increase in the ratios P^*/P and n^*/n and finally in a strong enhancement of the nuclear spin selectivity of the microwave-induced recombination. This way is believed to be the most effective in isotope fractionation and even in isotope purification. An inspiring argument is also that this way might be experimentally rather easily realizable.

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(6) The number of encounters of a selected radical with its partner in 1 s is $k_{\mathrm{reen}}C$, where "concentration" of partner obeys the simple relation $C = V^{-1}$ (one partner in the microreactor of volume $V = (4/3)\pi L^3$). On the other hand, $k_{\mathrm{reen}} = 4\pi RD$, where $R = r_1 + r_2$, $D = D_1 + D_2$, r_1 and r_2 are the radii of the radical and its partner, respectively, and D_1 and D_2 are their diffusion coefficients. Combining these relations and taking into account $\tau_{\mathrm{reen}} = (k_{\mathrm{reen}}C^{-1})$, we obtain the relation $L^3 = 3RD\tau_{\mathrm{reen}}$.

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