Magnetic probing of transition states

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The concept of dynamic trajectories on the potential energy surface of magnetic and exchange interactions for cage reactions in a radical pair is formulated. The magnetic effects induced by static as well as by a combination of static and radiowave magnetic fields are considered as tools for magnetic probing of the exchange potential along the dissociating bond. Transition state radiospectroscopy as an analogue to the transition state femtosecond spectroscopy, developed by Zewail, is suggested.

1. Introduction

Spin selective chemical reactions are a powerful source of beautiful magnetic effects induced both by static magnetic fields (magnetic field effects, MFE [1–4]; magnetic isotope effects, MIE [1–4]; chemically induced dynamic nuclear polarization, CIDNP [5]; chemically induced dynamic electron polarization, CIDEP [6,7]) and by combinations of static and radiowave magnetic field (reaction yield detected magnetic resonance, RYDMR [#1]; optically detected magnetic resonance, ODMR [9]; stimulated nuclear polarization, SNP [10]; radio induced magnetic isotope effect, RIMIE [11]).

All these effects depend on kinetic phenomena and are based on the dynamic behaviour of the pair of electron spin carriers, particularly, of the radical pair, one of the most important and widely investigated intermediates in radical reactions.

The scale of the magnetic effects is determined by three fundamental dynamics. The leading role belongs to spin dynamics: the time evolution of the spin states of the prereactive pairs driven by magnetic interactions. For radical pairs it is triplet–singlet conversion induced by Zeeman and hyperfine interactions as well as by spin relaxation; the former are responsible for the coherent contribution to the spin evolution while the latter is responsible for the in-

coherent contribution. For simplicity and without any loss of generality we will further discuss the dynamic evolution of the radical pair.

Spin dynamics are superimposed on the molecular dynamics of the radical pair; it starts at the moment when one of the partners of the contact pair, assumed to be generated in a nonreactive triplet state, leaves the pair for diffusional trips of different distances and durations.

Even in nonviscous liquids there is a certain probability for the escaping partner to return and experience a reencounter with its primary partner, but, in restricted microreactors (micelles [#2], zeolite cavities [13] etc.) this chance is much higher. The path traversed by the radical from the moment of escape till reencounter is its diffusional trajectory and the time that the pair has spent on this trajectory is used by the pair for triplet–singlet spin evolution to prepare itself for recombination. If at the moment of reencounter the pair has managed to transform its triplet state into a reactive singlet one, it reacts (recombine, disproportionate, etc.), otherwise it starts on a new diffusional trajectory and so on.

Chemical dynamics, which is the third fundamental type of dynamics, characterizes the chance for the pair to be chemically alive. At the moment when any one partner reacts (by decomposition, atom abstrac-

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[#1] For a recent example, see ref. [8].

[#2] For an elegant example of micellized radicals pairs displaying correlated behaviour, see ref. [12].

tion or addition reactions) the pair dies, its spin and molecular dynamics stop and a new pair, with its own set of dynamics, is born.

Spin dynamics are modulated by molecular dynamics since the stochastic changes of interradical distances and mutual orientations of radicals on the diffusional trajectories induce stochastic changes in the magnitude and possibly, for some cases, the sign of exchange interradical interaction which is known to influence strongly the spin dynamics. In other words the diffusional trajectories of the radical pair are the dynamic trajectories on the potential energy surface of geminate radical pair reactions similar to dynamic trajectories widely exploited in the theories of chemical dynamics for, particularly, gas phase reactions [14]. The difference lies in the fact that the probability of a reencounter between the reactive fragments, after a diffusional excursion, in condensed phases and especially in restricted media, is nonnegligible, whereas in the gas phase this probability is virtually zero. This allows for the distance-dependent interactions to experimentally manifest themselves; especially when conducted in restricted spaces.

2. Magnetic nonequivalence of dynamic trajectories

Suppose that in a representative radical pair one of the partners R_0 is chemically fixed and the other, R_i, is allowed to change chemical structure and therefore magnetic characteristics (the type and the number of magnetic nuclei, hyperfine coupling constants, g factor, electron relaxation time). Undoubtedly, the dynamic trajectories for these pairs (R_0, R_i) are magnetically nonequivalent even in identical exchange potentials.

Much more intriguing is the case when R_i radicals are chemically, and therefore, magnetically equivalent. The question that deserves a critical examination is whether the dynamic trajectories for magnetically equivalent radical pairs can be magnetically nonequivalent. A positive answer is possible in principle because magnetic equivalency is destroyed by the exchange potential, i.e. spin dynamics are different in different exchange potentials even for magnetically equivalent radical pairs. For example, short distance and long distance trajectories are nonequi-

valent even for identical pairs since their spin evolution takes place in different potentials.

The problem of magnetic equivalence or non-equivalence of dynamic trajectories and of their discrimination is not rhetorical. If the different products of cage reactions are formed on different trajectories then the magnetic effects detected for these products should be different and can be considered as a tool to assign different trajectories to different cage reactions and vice versa.

To illustrate this behaviour we will consider the magnetic behaviour of the chemical yield for different cage reaction products from the photolysis of optically active methyldeoxybenzoin 1 (scheme 1).

The results of the photolysis are the photodecomposition of the starting ketone 1, the loss of optical activity due to molecular reorientation of the radicals in the intermediate triplet radical pair followed by its recombination with regeneration of the ketone in two stereoisomeric forms S or R with probabilities of formation P_+ and P_-, respectively. In addition to ketone regeneration by recombination, benzaldehyde (PhCHO) is formed through disproportionation and p-ethyl-benzophenone is formed as a result of para head-to-tail addition of an acyl radical to the sec-phenethyl radical followed by isomerization of the quinoid structure into a p-substituted benzophenone (scheme 2).

A kinetic analysis of the loss of optical activity according to scheme 1 results in

$$\ln(a/a_0) = \beta \ln(1-f) , \qquad (1)$$

similar to the well-known equation for isotope enrichment due to the magnetic isotope effect [15]. Here a_0 and a are the optical activities of the starting ketone before and after photolysis, and f is the conversion for the ketone. The yield of benzaldehyde Y_{BA} and the β coefficient can be expressed in terms of the recombination and disproportionation probabilities, P_r and P_d,
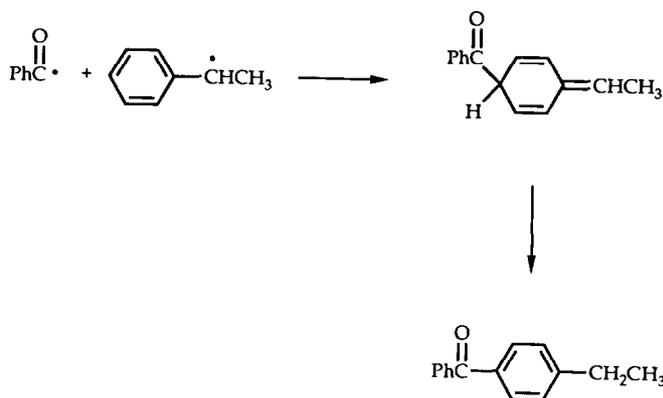
$$\beta = P_r/(1-P_r), \quad Y_{BA} = P_d/(1-P_r) . \qquad (2)$$

Both P_r and P_d are magnetic field dependent, since in the radical pair there is a competition between spin selective and therefore magnetically sensitive cage reactions (recombination and disproportionation) and spin nonselective escape.

The probability P_r in eq. (2) is taken as the sum
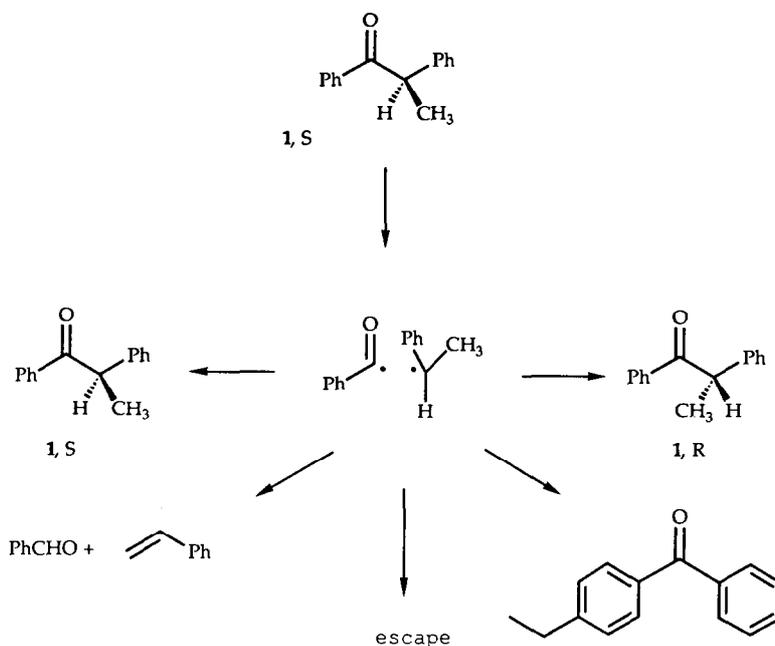
Scheme 1

Scheme 2

$(P_+ + P_-)$ under the very important condition

$$P_+ = P_- .$$

This condition implies that the dynamic trajectories for both recombinations to give the S and R stereoisomers are magnetically equivalent; the physical reasoning for this implication is that the rate of rotational molecular motion is much faster than the rate of triplet–singlet conversion so that the radical pair loses its stereochemical and therefore optical memory long before the triplet–singlet conversion is completed.

The loss of optical activity and the yield of benzaldehyde as a function of magnetic field were measured experimentally [15]. Two results of this paper are of crucial importance: (1) In spite of the fact that both probabilities P_r and P_d are strongly magnetic field dependent, these dependencies are similar and

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therefore the ratio P_r/P_d is independent of the magnetic field (fig. 1). (2) The circular dichroism of the micellar solutions of the starting ketone, that measures the difference in concentrations of the R and S enantiomeric forms, decreases during the photolysis due to racemization; however, there is no influence of the magnetic field on the decrease (fig. 2). It proves unambiguously that the radical pair regen-
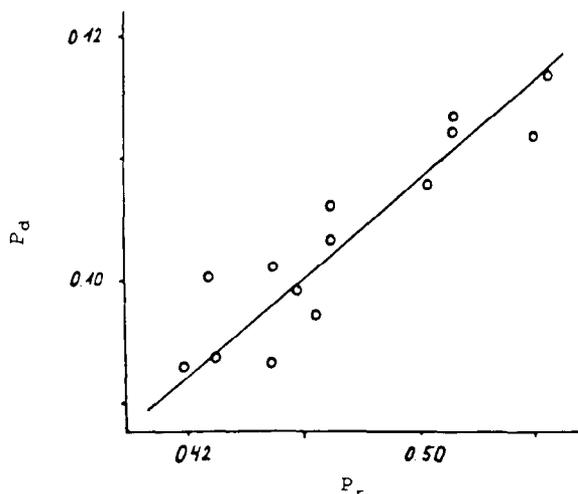

Fig. 1. Correlation between the recombination (P_r) and disproportionation (P_d) probabilities of the radical pair derived from methyldeoxybenzoin in SDS micelles (magnetic fields range from 0 to 1500 G).
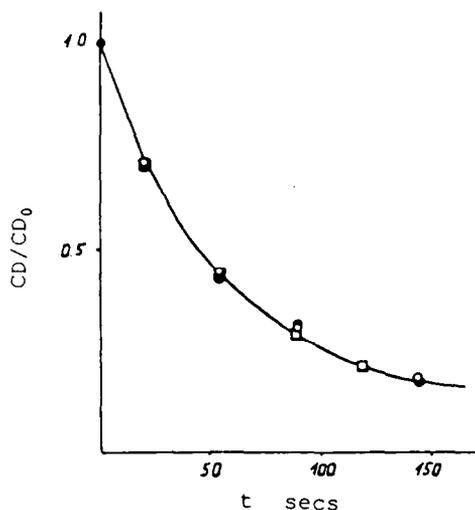

Fig. 2. Strength of the circular dichroism signal as a function of photolysis time at different magnetic fields; (O) 0 G, (●) 0.1 kG, (□) 1.8 kG.

erates the R and S enantiomeric ketones with equal probabilities, $P_+ = P_-$.

We can conclude that the dynamic trajectories for both R and S head-to-head recombinations and for disproportionation are magnetically equivalent; that is, the magnetic prehistory for both cage reactions is identical. Recently strong evidence in favour of the magnetic equivalence of the two head-to-head recombinations with regeneration of the d, l and meso diastereomeric forms, even for short lived radical pairs, was presented in the photolysis of d,1-2,4-diphenylpentan-3-one [16].

Now we turn to isotope enrichment of the cage products. For the kinetic scheme

$$M \underset{P_r}{\overset{h\nu}{\rightleftharpoons}} RP \left.\begin{array}{l} \longrightarrow \text{escape} \\ \\ \longrightarrow B \end{array}\right.$$
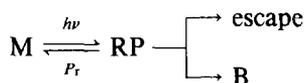
the isotope enrichment of the reversibly regenerated ketone [17] molecule M is given by

$$\ln(\delta_m/\delta_0) = (1-\alpha_m)\ln(1-f^*) , \qquad (3)$$

where δ_m and δ_0 are ^{13}C content in the ketone after and before photolysis and f^* is the conversion achieved;

$$\alpha_m = (1-P_r)/(1-P_r^*) , \qquad (4)$$

where P_r^* and P_r are the recombination probabilities for magnetic, with ^{13}C in CO group of acyl radical, and nonmagnetic radical pairs.

For the enrichment of "nonreversible" products B, such as benzaldehyde or p-ethylbenzophenone, the relation

$$\delta_b/\delta_0 = (\alpha_m/\alpha_b) (f^*/f) \qquad (5)$$

is valid, where δ_b is the ^{13}C content in B, f is the conversion of nonmagnetic ketone, with ^{12}C in CO group, and

$$\alpha_b = P/P^* . \qquad (6)$$

P^* and P are the probabilities of formation of B from magnetic and nonmagnetic RPs respectively [18].

The isotopic compositions of the starting ketone, benzaldehyde and p-ethylbenzophenone were measured experimentally as a function of conversion and the probabilities P and P^* were determined. The most striking result is the different isotopic compositions of the two B products which are shown in fig. 3, as
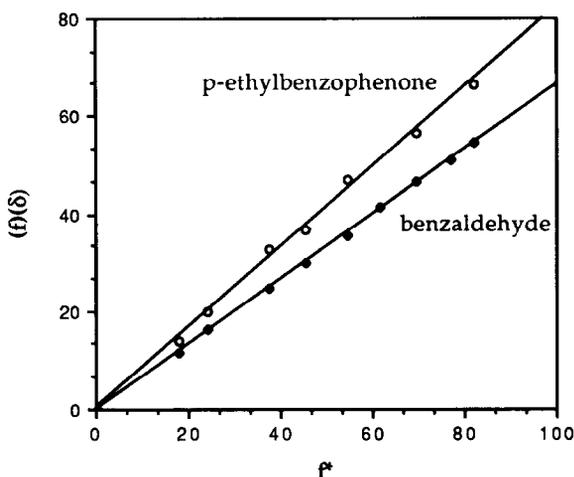
Fig. 3. Product of conversion and isotope content in *p*-ethyl-benzophenone and benzaldehyde as a function of conversion of labeled material.

a function of conversion, in terms of eq. (5). This is evidence for the different ratios P/P^* for benzaldehyde and *p*-ethyl-benzophenone:

$$(P/P^*)_{\text{benzaldehyde}} = 1.24 (P/P^*)_{p\text{-ethylbenzophenone}} \, .$$

This is a remarkable result which unambiguously indicates that the dynamic trajectories for the head-to-tail recombination are magnetically nonequivalent to the head-to-head reaction trajectories. So it has, indeed, been shown that different dynamic trajectories may be responsible for the different cage reactions even for chemically identical radical pairs.

The physical reasoning for such effects seems to be evident if we suppose that head-to-tail recombinations predominate on long distance trajectories with relatively low average exchange potential in comparison with head-to-head reaction trajectories. The exchange potential is known to depress the spin evolution induced by HFI so that the long distance–low exchange trajectories result in higher isotope enrichment of *p*-ethyl-benzophenone with respect to benzaldehyde in accordance with the experimental observations.

Although this is the first instance, to the best of our knowledge, of such nonequivalent magnetic trajectories being detected for radical pairs, we must acknowledge that conceptually and experimentally this idea has precedent in the field of triplet biradicals.

Both Doubleday [19–23] and deKanter and Kaptein [24] recognized that such a concept could be used to rationalize the S_0–T component observed in the field dependent CIDNP spectra of short and medium chain acyl–alkyl biradicals. Specifically, they postulated and realized that intersystem crossing by spin–orbit coupling, a nuclear spin independent process, in the triplet radical pairs could have different efficiencies for different conformations of the biradical. This is the conceptual equivalent of the suggestion that our result is the manifestation of a hyperfine induced intersystem crossing that is modulated by an exchange potential which is dependent on geometric considerations.

Similarly, the different isotopic enrichments observed in the different products of recombination from the biradicals derived from α,α'-diphenylcycloalkanones by Doubleday and co-workers [25] has been rationalized on the basis of a larger contribution of spin–orbit coupling to intersystem crossing in those biradical conformations where the end-to-end distance between the biradicals is shorter. Scaiano [26] has also invoked the concept of different rates of intersystem crossing in different conformations of triplet biradicals to explain the effects of solvents and paramagnetic quenchers on the lifetimes of the biradicals in different fluid media.

Along with the concept of magnetic nonequivalence of dynamic trajectories it is instructive to discriminate between short and long trajectories with respect to space and time. Short-in-time and short-in-distance trajectories are not necessarily identical. This remark concerns itself with most of the molecular systems with restricted motions such as radical or ion–radical pairs or biradicals in micelles, zeolite cavities, liquid crystals etc. Van der Waals and Coulomb potentials, as well as conformational restrictions determine, for the molecular systems, the choice of dynamic trajectories. The choice is wide, for instance, for a free radical pair in homogeneous solution but strongly restricted for short bridged biradicals [19–26].

3. Magnetic probing of transition state

Different dynamic trajectories for different cage reactions, and therefore for different cage products,

result in the differentiation of magnetic effects for various cage products. In other words, experimentally observed magnetic effects carry the fingerprints of dynamic trajectories, the fitting of theory to experiment providing a means to reproduce quantitative parameters of the averaged cage product dynamic trajectory. Some of these parameters, for example HFI constants and g factors are known; others, like T_1 relaxation times, and in particular, the most important, exchange potentials are extracted from the fitting procedure. One may point to ref. [15], in which $J(r)$ was found along the $\alpha(C-C)$ bond for methyldeoxybenzoin, as a successful example of such fitting.

The strategy of magnetic probing of exchange potential along the reaction coordinate of formation or dissociation of the chemical bond is an important supplement to the transition state spectroscopy, developed recently by Zewail and co-workers [27], based on femtosecond time resolved optical spectroscopy. The difference is that femtosecond spectroscopy probes the transition state of the dissociation reaction at exchange potentials $J \gg kT$, while the magnetic probing deals with the exchange potential at long interatomic distances at $J \ll kT$.

The magnetic probing of the transition state manifests itself either in magnetic effects induced by static magnetic fields or in magnetic effects induced by radiowave magnetic fields such as SNP or RIMIE for instance. The latter can be considered as a transition state radiospectroscopy in analogy with Zewail's transition state optical spectroscopy.

The concept of magnetic probing and magnetic equivalence or nonequivalence of dynamic trajectories is supposed to be fruitful for understanding the many details of radical reactions in organized media (micelles, zeolites, etc.) and for effective perturbations of the dynamic trajectories by radiofrequency irradiation to induce new magnetic effects.

Acknowledgement

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