Soviet Scientific Reviews, Section B

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Edited by

M. E. VOL'PIN

Institute of Organometallic Elements, Moscow

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SOVIET SCIENTIFIC REVIEWS

Советские Научные Обзоры

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Preface to the Series

In the last few years many important developments have taken place in Soviet science which may have not received as much attention as deserved among the international community of scientists because of language problems and circulation problems.

In launching this new series of *Soviet Scientific Reviews* we are motivated by the desire to make accounts of recent scientific advances in the USSR more readily and rapidly accessible to scientists who do not read Russian. The articles in these volumes are meant to be in the nature of reviews of recent developments and are written by Soviet experts in the fields covered. Most of the manuscripts are translated from Russian. In the interest of speedy publication neither the authors nor the volume editors have an opportunity to see the translations or to read proofs. They are therefore absolved of any responsibility for inaccuracies in the English texts.

Soviet Scientific Reviews will appear annually, with the average of specific subject areas in each of the sciences varying from year to year. In 1979 we are publishing volumes in Chemistry and Physics. In subsequent years we plan to expand the series with the addition of annual volumes in Mathematics, Biology, and Space Science.

We are much indebted to the volume editors and individual authors for their splendid cooperation in getting these first volumes put together and sent to press under considerable time pressure.

The future success of this series depends, of course, on how well it meets the readers' needs and desires. We therefore earnestly solicit readers' comments and particularly suggestions for topics and authors for future volumes.

By taking this initiative we hope to contribute to the development of scientific cooperation and the better understanding among scientists.

Foreword

Soviet Scientific Reviews is a new and interesting initiative providing scientists everywhere with rapid communication of research by their Soviet colleagues, avoiding the language barrier.

This volume, which I have the honor of introducing, outlines such advances in various branches of chemistry. Since the field of research in chemistry is extremely broad, the choice of topics is to some extent inevitably personal. Nevertheless our intention is to reflect the most important developments in chemistry in our country within the first volume.

In this inaugural volume, two reviews deal with modern aspects of catalysis, viz. physiochemical aspects of enzyme action and new interesting data on heterogeneous catalysis. The paper on mechanism of reactions involving organometallic species presents new achievements of a well-known Soviet scientific school. An interesting review is devoted to a rather new field of research, namely, the effect of magnetic fields on chemical reactions—a problem of great importance not only for chemistry but for biology as well.

In the interest of speed of publication authors have not seen proof and are therefore not responsible for translation or technical errors which might occur.

I hope that this new initiative in making Soviet research results quickly available to the scientific community will be well received and that it will attract a wide circle of readers.

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M. E. Vol'pin
Moscow, March 1979

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Effect of Magnetic Field on Radical Reactions in Solution

Yu. N. Molin, R. Z. Sagdeev, and
K. M. Salikhov

*Institute of Chemical Kinetics and Combustion,
Academy of Sciences of the USSR,
Siberian Branch,
Novosibirsk, 630090, USSR.*

Contents

1. Introduction

The search for magnetic field effects in the kinetics of chemical reactions has been conducted since the end of the last century. However, the number of systems in which these effects have been observed so far is very limited.

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In 1913, the effect of the magnetic field on fluorescence of iodine vapor was observed.[1] Franck and Grotrian attributed this effect to the change in the rate of the competing nonradiative process in the magnetic field—magnetic predissociation.[2] Since then magnetic predissociation of molecules has attracted the widespread attention of investigators (see, for example, Refs. 3-8). The effect of the magnetic field on luminescence of more complex molecules was recently observed.[9-12] However, the iodine molecule remains the only example for which the mechanism of the magnetic field effect is understood in every detail.

The effect of magnetic predissociation on the chemical reaction rate was observed by Falconer and Wasserman,[13] who discovered that photo-isomerization of 2-butene catalyzed by I_2 pairs can be accelerated by applying an 85-kG magnetic field.

The magnetic effects in heterogeneous catalytic reactions have attracted the attention of many investigators, but these studies, except for those of ortho/para-conversion of hydrogen,[15,16] have not yielded any reproducible results (see, for example, Ref. 14).

Another interesting example of the effect of magnetic field on physicochemical processes is the acceleration of the annihilation of positronium.[17] The Zeeman interaction between positronium and the magnetic field combines ortho- and para-states, and thereby decreases the lifetime of the long-lived triplet state.

The search for the effect of the magnetic field on reactions in solutions has, with a few exceptions, yielded negative results, and reported observations of this effect frequently could not be confirmed by subsequent experiments. In his review paper[18] on research up to 1945, Selwood mentioned only one study[19] in which the effect of the magnetic field on homogeneous reaction rates was observed. Effects of the order of several percent were observed in the reactions in which the total magnetic susceptibility of the system varied. Although this work subsequently was cited in many papers, the results remained in question. Kazakov[20] could not confirm this effect by repeating the experiments for two reactions, which, according to the data of Bhatnagar et al.,[19] were most sensitive to the magnetic field. Selwood also reported on his attempt to reproduce some results of the patent literature on the control of chemical reactions by magnetic field. Negative results were obtained in all cases.

Reported observations of magnetic field effects, unconfirmed by other authors, have been published periodically. Schmid et al.[21] reported an eightfold decrease in the polymerization rate of styrene in a 16-kG field

at 80°C. Collins et al.,[22] however, could not reproduce this effect. The magnetic field also had no effect on the decomposition rate of benzoyl peroxide[23] —the initiator of styrene polymerization.

This situation produced a skeptical attitude toward the problem as a whole, further complicated by a prolonged dearth of ideas about possible physical mechanisms which might show a noticeable effect of the magnetic field on chemical reactions in solutions. The possibility of disturbing chemical equilibrium by varying magnetic susceptibility in a reaction was theoretically investigated.[24] Under most favorable conditions the relative variation of the equilibrium constant did not exceed 10^{-4} at room temperature.

The effect of the directive action of the magnetic field on electron spins of free radicals or other paramagnetic particles has been the subject of many discussions. However, under ordinary experimental conditions (room temperature, magnetic field up to 10 kG) the Boltzmann difference in the probabilities of different spin orientations is too small to produce noticeable effects.

Finally, the possibility of orienting the molecules in the magnetic field, which in one way or another can influence their chemical reactivity, was investigated. As indicated by Dorfman,[25] this effect can be significant for very large molecules (or conglomerates of molecules) with anisotropic magnetic susceptibility (for example, DNA molecules, reactions in liquid crystals). Although the effect of magnetic field on reactions in liquid crystals has been experimentally observed,[26] it is generally considered to be negligible.

As a result, about a decade ago many investigators assumed that, with the possible exception of biological systems, reactions in solutions are not noticeably affected by the magnetic field. Recently, however, the situation has changed radically because of the observation of two effects. First, magnetic effects were discovered in processes that involve triplet excitations in solids[27–29] (these processes are discussed in detail in a review paper by Sokolik and Frankevich[30]). These studies gave impetus to the search for analogous effects in solutions. Secondly, the discovery of chemical polarization of nuclei,[31,32] and its explanation,[33,34] led Lawler and Evans[35] to assume that the magnetic field can affect radical reactions in solutions.

In recent years, a number of experimental studies have been conducted to demonstrate the effect of the magnetic field on chemical reactions of free radicals. A fairly accurate theory of the effect of the magnetic field on the rates of these processes has been developed; the key

feature of this theory is allowance for the spin selection rules in the recombination reaction and for the cage effects which are characteristic of the reactions in solution. In this review paper we summarize the results of these studies (see also Refs. 36 and 37).

2. Physical Model

The radical reactions are the largest class of chemical reactions in which the magnetic field can be expected to have an effect. As is well know now, this effect can occur during the recombination reaction* of two radicals in a single "cage," which form a radical pair (RP). The term cage, used in a broad sense, is a certain region of effective recombination of the radicals of a given pair.[38] As long as there are two radicals in this region, the probability of their reaction with the other molecules is negligible compared to that of their recombination with each other. The theory of radical reactions in solutions distinguishes between two cases of recombination in a cage. The first case is a recombination of correlated radical pairs, i.e., radical pairs in a definite spin state—either singlet or triplet. Such radical pairs are formed, for example, as a result of a monomolecular decomposition due to the action of heat, light, or ionizing radiation. The second case is a reaction of uncorrelated radical pairs (the so-called F-pairs), in which two radicals are recombined as a result of a random encounter. In these pairs the statistical weight of the singlet state is equal to $1/4$ and that of the triplet state is equal to $3/4$. Since the recombination reaction of a radical pair is spin selective and, as a rule, proceeds from the singlet state, the probability of the reaction will vary if its multiplicity varies in the cage during the lifetime of the radical pair (see Fig. 1a).

Thus a triplet radical pair can recombine only after a $T \rightarrow S$ transition. Conversely, if the original radical pair is in the singlet state, then the $S \rightarrow T$ transitions will cause the radical pairs to go into the nonreactive triplet state, which will decrease the recombination probability.

Note that one of the spin states (the triplet state in the example discussed above) need not necessarily be nonreactive in order to observe the effect of the S-T transitions on the yield of the products. If the states of the radical pairs with different spin multiplicity yield different recombi-

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*The term "recombination," used here in a broad sense, includes disproportionation reactions.

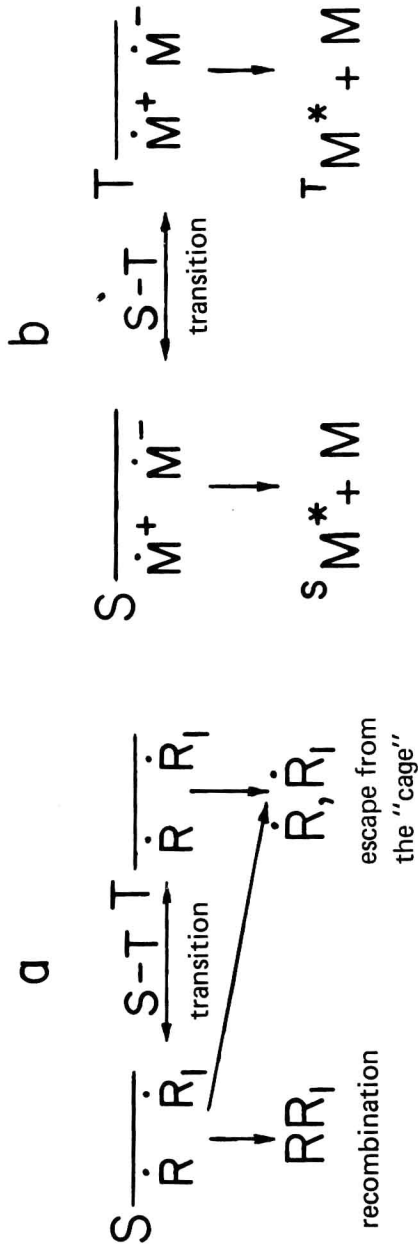**Figure 1.** a) Scheme of the processes accompanying the radical-pair recombination in the cage. The recombination of a singlet radical pair decreases because of the S → T transition. The triplet radical pair can recombine only after the T → S transition. b) Scheme of the reactions accompanying the recombination of aromatic radical ions. The ratio of the singlet and triplet excited molecules depends on the S-T transition rate.

nation products, then their ratio will also vary in the presence of S-T conversion. An example of such a system is the recombination of a ~ of aromatic ion-radicals in a solution. Depending on the multiplicity of the pair, either a singlet or a triplet excited molecule will be produce a result of recombination, and their ratio will depend on the rate of singlet-triplet transitions of the pair (Fig. 1b).

Let us discuss in more detail the mechanisms of the singlet-triplet (S-T) transitions in the radical pairs, because, according to the results of a theoretical study, these transition rates may be sensitive to the external magnetic field. In contrast to singlet-triplet transitions in the molecules, where the spins of the corresponding electrons are fixed by the strong exchange interaction, the exchange interaction in radical pairs decreases rapidly with increasing distance between the radicals. The singlet-triplet pair evolution is most effective at distances where the exchange interaction can be disregarded and where the spins of the electrons precess independently in the external field.

Under these conditions the S-T transitions in the pair can be attributed either to the difference in the Larmor precession frequencies of the electron spins (Δg mechanism) or to the influence of hyperfine coupling with the nuclei of the radicals (HFC mechanism).

First, we shall examine the Δg mechanism, i.e., a situation in which the radicals do not have nuclear magnetic moments but their Larmor precession frequencies $\omega_i = g_i \beta \hbar^{-1} H_o$ are distinguishable in the external magnetic field H_o. It can be seen from the simple vector model that during the precession transitions will take place between the singlet state and one of the triplet states T_o, which has a zero projection of the total electron spin on the external field. In fact, the singlet spin state of a radical pair can be expressed schematically as two magnetic moments precessing around the field H_o in such a way that their sum will be equal to zero (Fig. 2a). Since in the triplet state the total spin of a radical pair is equal to 1, the state T_o can be expressed by using the model in Figure 2a. If the Larmor precession frequencies of the spin moments of the radicals of a pair are different, then during the precession transitions will periodically take place between two reciprocal vectors shown in Figure 2a, i.e., a difference in the Larmor frequencies of the spins of a radical pair leads to S-T_o conversion. The frequency of these transitions is proportional to the difference in the Larmor frequencies of the radicals of a pair and increases linearly with the intensity of the constant external magnetic field. It follows from this that the Δg mechanism does not lead to the transitions to two other triplet states T_+ and T_-.
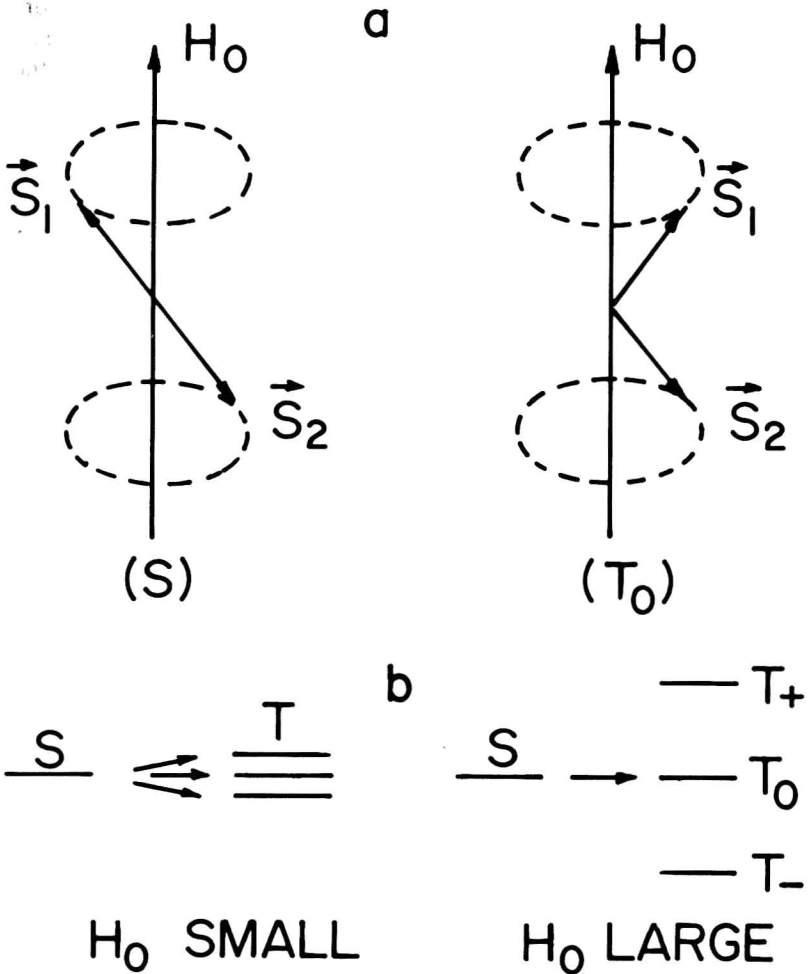
Figure 2. Scheme of the S-T transitions. a) Δg mechanism. A difference in the Larmor precession frequencies of spins S_1 and S_2 leads to transitions between S and T states of the radical pair. b) HFC mechanism. In a weak field, hyperfine coupling induces transitions to all three triplet states; in a strong field, which eliminates the degeneracy of triplet levels, it leads to a transition only to the T_0 state which is in resonance with S.

The HFC mechanism of the conversion of radical pairs in strong magnetic fields ($\geqslant 1$ kG) is similar to the Δg mechanism: the induced local HFC field, upon combining with the external field, produces a difference in the precession frequencies of the spin angular momenta of the unpaired electrons of the radical pairs, which gives rise to the S-T_0 transition. However, a basic difference between these two mechanisms can be observed in weak external magnetic fields which are comparable to the local field: the hyperfine coupling begins to induce transitions from the singlet state to all three triplet states. A qualitative difference of the HFC mechanism is attributable to the fact that the spin magnetic moments of the unpaired electrons of the radical pair precess around the total external and local (HFC) fields. Since in strong external fields the direction of the total field practically coincides with that of the external magnetic field, the projections of the spin angular momenta of the electrons on H_0 are conserved. In weak fields, however, the direction of the total field does not coincide with that of the external field; as a result, transitions can take place not only to the T_0 state but also to the $T_{\pm}$ state (see Fig. 2b).

Thus two basic mechanisms, the Δg and HFC mechanisms, of the effect of external magnetic field on the kinetics of radical chemical reactions have now been accepted. In the first case, the interaction responsible for singlet-triplet transitions of radical pairs in the cage increases with increasing field intensity. In the second case, the field effect is linked to the dependence on the field intensity of the number of effectively working channels for the singlet-triplet transitions of radical pairs in the cage.

The efficiency of the singlet-triplet transitions in radical pairs induced by the hyperfine coupling should be different for isotopes with different nuclear magnetic moments. Therefore, another interesting and important magnetic effect, the isotopic effect, can take place in the radical reactions in addition to the external magnetic field effect.

The external magnetic field effect and the isotopic effect in the radical reactions are attributable to molecular and spin dynamics of radical pairs in the cage. The molecular motion of partner reagents in condensed media is such that they remain in the cage a relatively long time. For example, the lifetime of neutral radicals in the cage is $\sim 10^{-9}$ sec in liquids with a diffusion coefficient of $\sim 10^{-5}$ cm^2/sec.[38] This relatively long time allows weak spin-spin interactions of unpaired electrons, such as the hyperfine interactions to occur. The conditions for occurrence of magnetosensitive S-T transitions in radical pairs can be improved by increasing the lifetime of the radical pairs in the cage. This can be accomplished

by increasing the viscosity of the solution. If radical ions are the partners, then the size of the cage, which is determined by the Onsager radius, can reach hundreds of angstroms in weakly polar solutions. In this case, highly favorable conditions can be established for an effective singlet-triplet mixing in a radical pair.

Brocklehurst examined another possible mechanism for the effect of magnetic field on S-T transitions, which can be called a relaxation mechanism.[39] This mechanism is based on the principle of the dependence of the time of paramagnetic relaxation, which apparently is accompanied by a change in multiplicity of the radical pairs, on the magnetic field intensity. At present, it is clear that this mechanism usually is much less effective for free radicals than the Δg and HFC mechanisms examined above. The relaxation mechanism, however, may become dominant for systems with short relaxation times. Such situations occasionally occur in the case of free radicals, but are typical if one of the partners of the pair is a transition-metal ion or a triplet molecule. Note that the theory of the effect of the magnetic field on quenching of excited triplet states in solutions essentially uses the relaxation mechanism.[40]

3. Singlet-Triplet Evolution of Radical Pairs

Let us examine in greater detail the spin motion of radical pairs. The spin-Hamiltonian of the radical pairs (1)

$$\hat{H} = g_A \beta H_o \hat{S}_{AZ} + g_B \beta H_o \hat{S}_{BZ} + \hbar \sum_i^{(A)} A_{Ai} \hat{S}_A \hat{I}_i + \hbar \sum_K^{(B)} A_{BK} \hat{S}_B \hat{I}_k - \hbar J(r_{AB})(1/2 + 2\hat{S}_A \hat{S}_B) \qquad (1)$$

includes the Zeeman energy, the hyperfine coupling, and the exchange interaction of the radicals. Since the exchange interaction depends on the distance between the radicals, we generally cannot consider separately spin and molecular dynamics. If, however, we are concerned with the spin evolution at relatively large distances between the radicals, when $J(r_{AB}) < A_A, A_B$ (during the intervals between re-encounters), then the exchange interaction has a negligible part and the spin evolution can be studied independently of the molecular motion of the reagents. In this approximation the spin-Hamiltonian of the radical pairs is given by