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# The Influence of the Magnetic Field on Processes Involving Radicals and Triplet Molecules in Solutions

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The results of studies of the influence of a constant magnetic field on reactions involving free radicals and triplet molecules in solutions are examined and the theoretical principles of the influence of the magnetic field on the recombination processes of free radicals (taking into account the spin effect) and the quenching of triplets are described. The theoretical models are compared with experimental data.
The bibliography includes 95 references

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## I. INTRODUCTION

The research on the effects of the magnetic field in the kinetics of chemical reactions has been prosecuted since the end of the last century. Nevertheless, the range of systems in which reliable effects have been observed has been very limited until recently.

The influence of the magnetic field on the fluorescence of iodine vapour was observed in 1913.[1] This effect was interpreted by Franck and Grotrian[2] as a result of the changed rate in the magnetic field of a competing non-radiative process—magnetic predissociation. Since then, the magnetic predissociation of molecules has continued to attract the attention of investigators (see, for example,

Refs. 3–8). However, iodine molecules are apparently still the only example for which magnetic predissociation has been investigated experimentally.

The direct influence of magnetic predissociation on the rates of chemical reactions has been observed by Falconer and Wasserman[9], who noted that the photoisomerisation of but-2-ene catalysed by $I_2$ vapour is accelerated following the application of an 85 kG magnetic field.

The magnetic effect in heterogeneous catalytic reactions has attracted the attention of investigators, However, these studies did not lead to reproducible results (see, for example, Figueras Roca[10]), with the exception of the *ortho–para* conversion of hydrogen[11,12].

Yet another interesting example of the influence of the magnetic field on physicochemical processes is the acceleration of the destruction of positronium[13]. The Zeeman interaction of positronium with the magnetic field mixed the *ortho*- and *para*-levels and thereby reduces the lifetime of the long-lived triplet state.

Research into the influence of the magnetic field on reactions in solution has so far yielded negative results as a rule and the reported observation of the effect has frequently not been confirmed by subsequent experiments. In his review[14] of studies up to 1945, Selwood noted only one investigation[15] where the effect of the magnetic field on the rate of homogeneous reactions had been observed. Effects amounting to several per cent have been found in reactions during which the overall magnetic susceptibility of the system changed. This study was subsequently quoted in many communications, but even these results have been questioned. On repeating the experiments for two reactions which have been stated[15] to be most sensitive to the magnetic field, Kazakov[16] failed to confirm the effect. Selwood also reported[14] that he had attempted to reproduce certain results in the patent literature concerning the control of chemical reactions by the magnetic field. Negative results were obtained in all cases.

Reports concerning the observation of effects due to the magnetic field, which were not confirmed by other workers, were also published subsequently. Thus, Schmid et al.[17] reported the retardation by a factor of 8 of the polymerisation of styrene in a 16 000 G field at 80°C, but Collins and Bryce[18] were unable to reproduce this effect. Nor did the magnetic field affect the rate of decomposition of benzoyl peroxide[19]—the inhibitor of the polymerisation of styrene.

This situation led to scepticism concerning the problem as a whole. This was also promoted by the prolonged absence of any ideas concerning the possible physical mechanisms for an appreciable influence of the magnetic field on chemical reactions in solution. The possibility of the displacement of the chemical equilibrium owing to a change in magnetic susceptibility during the reaction has been considered theoretically[20]. Even under the most favourable conditions, the relative change in the equilibrium constant did not exceed $10^{-4}$ at room temperature according to these estimates.

The idea of the orienting effect of the magnetic field on the electron spins of free radicals or other paramagnetic species has been frequently discussed. However, under the usual experimental conditions (room temperature, magnetic field up to 10 000 G), the Boltzmann difference between the probabilities of different spin orientations is too small to result in appreciable effects.

The possibility of the orientation of molecules as a whole in the magnetic field, which might have influenced in some way their chemical reactivity, was considered finally. This effect has been shown[21] to be significant only for very large molecules (or conglomerates of molecules) with an anisotropic magnetic susceptibility (for example, the DNA molecules and for reactions in liquid crystals). The influence of the magnetic field on reactions in liquid crystals has been observed experimentally[22], but in the general case this effect cannot play an appreciable role.

In view of all the above considerations, ten years ago the majority of investigators believed that the magnetic field cannot have an appreciable influence on reactions in solutions, with the possible exception of biological systems. However, recently the attitude to this problem has changed radically. This was promoted by the observation of two phenomena. Firstly, magnetic effects were noted in processes involving triplet excitons in solids[23–25] (these problems are discussed in detail in the review by Sokolik and Frankevich[26]). The above studies stimulated research on analogous effects in solutions. Secondly, the phenomenon of chemically induced nuclear polarisation was discovered[27,29] and explained[29,30], which permitted the formulation of a clear-cut physical mechanism of the possible influence of the magnetic field on chemical radical reactions in solutions.

A number of experimental studies have been made in recent years on the influence of the magnetic field on the chemical reactions of free radicals and on processes involving triplet excited molecules in solutions. A fairly detailed theory of the effect of the magnetic field on the rates of these processes has been developed, an important feature of which involves allowance for cage effects characteristic of reactions in solutions. The results of these studies are summarised in the present review.

## II. THE MECHANISMS BY WHICH MAGNETIC FIELDS INFLUENCE CHEMICAL REACTIONS WITHIN THE FRAMEWORK OF THE MODEL OF THE "CAGE" RECOMBINATION OF RADICAL PAIRS

We shall consider initially radical reactions—the largest class of chemical reactions in which an effect of the magnetic field may be expected. It is now known that this influence can arise in the stage involving the recombination† of two radicals in a single "cage" and forming a radical pair (RP). The "cage" is understood in a fairly wide sense of the word—it is a region of effective recombination of the radicals of the given pair with one another[31]. As long as there are two radicals in this region, the probability of their reaction with other molecules is negligibly small compared with the probability of their recombination with one another. During their lifetime in the "cage", the radicals can undergo numerous repeated collisions. In the theory of radical reactions in solutions, two cases of cage recombination are distinguished. The first involves the recombination of correlated radical pairs, i.e. radical pairs in a definite spin state—singlet or triplet. Such radical pairs arise, for example, as a result of unimolecular decomposition under the influence of heat, light, or ionising radiation. The second case includes the reactions of non-correlated radical pairs (the so called F-pairs) where two randomly colliding radicals recombine. In such pairs, the statistical weight of the singlet state is 1/4 and that of the triplet state 3/4. The recombination reaction of radical pairs is selective with respect to the spin and as a rule takes place in the singlet

†The term "recombination" is used here in a wide sense and includes also disproportionation reactions.

state. The reaction probability therefore changes if the multiplicity of the radical pair is altered during its lifetime in the cage (see Fig. 1).

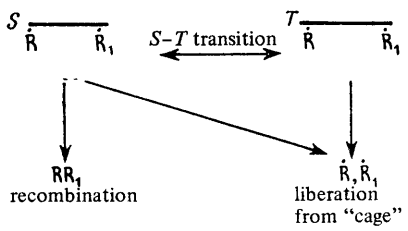



**Figure 1.** Schematic illustration of the processes occurring on recombination of radical pairs in the "cage". The efficiency of the recombination of a singlet radical pair decreases owing to the $S-T$ transition. A triplet radical pair can recombine solely after a $T \rightarrow S$ transition.

We shall consider in greater detail the mechanisms of singlet–triplet ($S-T$) transitions in radical pairs, since, according to the results of a theoretical study, the rates of these transitions can in fact be sensitive to the external magnetic field. Brocklehurst [32] put forward in 1969 the first idea, with a physical basis, concerning the possible mechanism of the influence of the magnetic field on singlet–triplet transitions in radical pairs. He examined the elementary process, typical for radiation chemistry, involving the recombination of an electron (or radical-anion) with its parent radical-cation. According to Brocklehurst [32], these two species form a singlet radical pair, since the initial ionisable molecule was in the singlet state. The transition of the pair to the triplet state can occur by the relaxation of electron spins. Since the electron paramagnetic relaxation times of radicals may depend on the magnetic field strength, the magnetic field may affect the ratio of the yields of the singlet and triplet excited molecules formed as a result of the recombinaton of these radical-ions. Although it is now clear that mechanisms leading to singlet–triplet transitions are more effective for free radicals or radical-ions, Brocklehurst's idea has not lost its importance for the prediction of field effects in systems with short paramagnetic relaxation times. It has been used in the development of a theory of the influence of the magnetic field on the quenching of excited triplet states in solutions [33].

A decisive step in the formulation of the most important mechanisms of $S-T$ transitions in radical pairs was made by Lawler and Evans in 1971, already on the basis of the advances in the field of chemically induced nuclear polarisation [34]. These investigators were the first to formulate the idea that the singlet–triplet transitions in radical pairs, invoked to account for chemically induced nuclear polarisation, must affect also the probability of the recombination of the radicals in the pair. They examined two mechanisms of the singlet–triplet transition in the pair: owing to the difference between the Zeeman frequencies of the radicals (the $\Delta g$ mechanism) and owing to the hyperfine interaction (the HFI mechanism) and showed that the efficiencies of the two mechanisms depend on the magnetic field strength. Subsequently these mechanisms were examined in detail in a number of studies. The manifestations of the $\Delta g$ mechanism [35–40] and the HFI mechanism [38,41–48] have been analysed.

Within the framework of the $\Delta g$ mechanism, the singlet state of the radical pair becomes mixed with only one of the triplet states $T_0$, having a zero projection of the overall spin of the unpaired electrons in the radical pair on the direction of the external magnetic field, i.e. only $S-T_0$ transitions are induced. This mechanism does not involve the two triplet states $T_{+1}$ and $T_{+1}$. The essential features of the $\Delta g$ mechanism for the evolution of the radical pair are illustrated in Fig. 2. The singlet spin state of the radical pair can be represented schematically by two magnetic moments processing about the direction of the field $H_0$ in such a way that their sum remains zero (Fig. 2*a*).

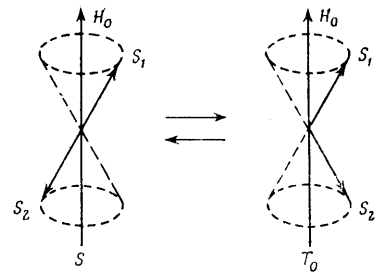



**Figure 2.** Schematic illustration of the $S-T_0$ transition via the $\Delta g$ mechanism. The difference between the Larmor precession frequencies of the $S_1$ and $S_2$ spins leads to transitions between the $S$ and $T_0$ states of the radical pair.

In the triplet state, the overall spin of the radical pair is unity and the $T_0$ state can therefore be represented in terms of the model illustrated in Fig. 2*b*). If the Larmor frequencies of the precession of the spin moments of the radical pair are different, then transitions between two reciprocal configurations of the vectors, shown in Fig. 2, will occur periodically during the precession, i.e. the difference between the Larmor frequencies of the radical pair spins leads to $S-T_0$ transitions. Their frequency is proportional to the difference between the Larmor frequencies of the radicals in the pair and increases linearly with the strength of the constant external magnetic field.

The manifestation of the HFI mechanism of the transitions of radical pairs in strong magnetic fields ($\gtrsim$1000 G) is similar to that of the $\Delta g$ mechanism: the local field induced by the HFI is combined with the external field and gives rise to a difference between the precession frequencies of the spin moments of the unpaired electrons of the radical pair, which leads to $S-T_0$ transitions. However, in weak external magnetic fields, comparable to the local field, a fundamental difference between the two mechanisms is observed: HFI begins to induce transitions from the singlet state to all three triplet states. The qualitative difference of the HFI mechanism is due to the fact that the magnetic spin moments of the unpaired electrons of the radical pair precess about the overall external and local (HFI) fields. In strong external fields, the direction of the overall field virtually coincides with that of the external magnetic field and the projection of the electron spin moments on to $H_0$ therefore remains the same. On the

other hand, in weak fields the overall field may not have the same direction as the external field, which results in the possibility of transitions not only to the $T_0$ state but also to the $T_{\pm 1}$ states.

Thus two fundamental mechanisms of the influence of the external magnetic field on the kinetics of chemical radical reactions have now been recognised: the $\Delta g$ and the HFI mechanisms. In the former case, the interaction, responsible for the singlet–triplet transitions in the radical pair in the cage, is itself intensified with increase of the magnetic field strength. In the second case, the field effect is associated with the dependence of the number of effectively operating channels for the singlet–triplet transitions in the radical pair in the "cage" on the magnetic field strength.

## III. DYNAMICS OF THE RADICAL PAIR SPINS

We shall now consider the singlet–triplet evolution of radical pairs. The following probability of the $S-T_0$ transition has been obtained for the $\Delta g$ mechanism [34-40]:

$$p_{ST_0} = \sin^2\left(\frac{1}{2}\Delta g\beta\hbar^{-1}H_0 t\right), \quad (1)$$

where $\Delta g$ is the difference between the $g$-factors of the radicals in the pair and $\beta$ is the Bohr magneton. Hence it is seen that the radical pair oscillates between the $S$ and $T_0$ states at a frequency

$$\omega_{ST_0} = |\Delta g|\beta\hbar^{-1}H_0. \quad (2)$$

For short times, when $\omega_{ST_0} t < 1$, the probability of the $S-T_0$ transition varies with the square of the magnetic field strength $H_0$:

$$p_{ST_0} \simeq \frac{1}{4}(g_1-g_2)^2\beta^2\hbar^{-2}H_0^2t^2. \quad (3)$$

Over a long time interval, where $\omega_{ST_0} t > 1$, there are on average equal contributions of the $S$ and $T_0$ states of the radical pair.

The singlet–triplet evolution of the radical pair in the case of the HFI mechanism is more complex, since under these conditions there is a possibility of transitions to all the triplet states and the transitions via different channels interfere with one another. Comparatively simple results are obtained only for short times, when $|A|t < 1$ ($A$ is the isotropic HFI constant) and the transitions via different channels are combined additively. In this case, the interaction of unpaired electrons with all the magnetic nuclei may be characterised by a single mean-square HFI constant [45]:

$$A_{\text{eff}} = \left\{\sum_k A_{1k}^2 + \sum_n A_{2n}^2\right\}^{1/2}, \quad (4)$$

where $A_{1k}$ and $A_{2k}$ are the HFI constants of the radicals in the pair. In a zero external magnetic field, the probability of the transition of the radical pair from the singlet to the triplet state is

$$p_{ST}^0 \simeq \frac{3}{16}A_{\text{eff}}^2 t^2. \quad (5)$$

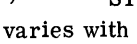
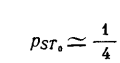
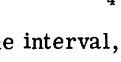
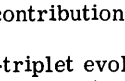
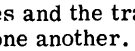
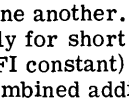
Correspondingly, the following expression has been obtained for strong fields when $g\beta\hbar^{-1}H_0 > A_{\text{eff}}$:

$$p_{ST_0}^{\infty} \simeq \frac{1}{16}A_{\text{eff}}^2 t^2. \quad (6)$$

Thus, for radical pairs with sufficiently short lifetimes, i.e. when the condition $A_{\text{eff}} t < 1$ holds, the ratio of the probabilities of the $S-T$ transitions in a zero field and in a strong field is 3, which corresponds exactly to the number of transition channels operating effectively in weak and strong fields.

For arbitrary lifetimes, the calculations of the probabilities of the $S-T$ transitions in radical pairs become more complex even in the two limiting cases of zero and strong fields. Calculations have therefore been made only for the simplest model radical pairs [41-47]. Table 1 presents the probabilities of the $S-T$ transitions for certain systems. As was to be expected, the calculations for short times yield $p_{ST}^0 = 3p_{ST_0}^{\infty}$. However, for comparatively long-lived radical pairs, a very remarkable feature of the HFI mechanism is observed: the probability of the $S-T$ transitions in weak fields, where three competing $S-T_0$, $T_{+1}$, $T_{-1}$ transition channels operate, is sometimes smaller than in strong fields where only one $S-T_0$ channel operates. Such anomalous properties are shown by radical pairs numbered V and VI in Table 1. This feature of the HFI mechanism is discussed in detail by Sarvarov and Salikhov [46].

Table 1. The probabilities of the $S-T$ transitions induced by the hyperfine interaction (nuclear spin $I = 1/2$).

| No. of pair | RP | $p_{ST}^0$ | $p_{ST}^{\infty}$ |
|---|---|---|---|
| I |  | $\frac{3}{16}\sin^2(At) + \frac{3}{4}\sin^2\left(\frac{A}{2}t\right)$ | $\frac{1}{2}\sin^2\left(\frac{1}{2}At\right)$ |
| II |  | $\frac{2}{3}\sin^2\left(\frac{3}{4}At\right)$ | $\frac{1}{2}\sin^2\left(\frac{1}{2}At\right)$ |
| III |  | $\frac{2}{3}\sin^2\left(\frac{\sqrt{3}}{4}At\right) + \frac{1}{3}\sin^2\left(\frac{\sqrt{3}}{2}At\right)$ | $\frac{1}{2}\sin^2\left(\frac{1}{2}At\right)$ |
| IV |  | $\frac{20}{27}\sin^2\left(\frac{3}{4}At\right) + \frac{4}{27}\sin^2\left(\frac{3}{2}At\right)$ | $\frac{1}{2}\sin^2\left(\frac{A}{2}t\right) + \frac{1}{8}\sin^2(At)$ |
| V |  | $\frac{3}{4}\sin^2\left(\frac{A}{2}t\right)$ | $\sin^2\left(\frac{A}{4}t\right)$ |
| VI |  | $\frac{15}{32}\sin^2(At) + \frac{3}{8}\sin^2\left(\frac{A}{2}t\right)$ | $\frac{1}{4}\sin^2\left(\frac{3}{4}At\right) + \frac{3}{4}\sin^2\left(\frac{A}{4}t\right)$ |

The above results were obtained on the hypothesis that the exchange interaction of the unpaired electrons of the radical pair is insignificant. This corresponds to the initial model where the $S-T$ transitions occur in the interval between two repeated collisions of the pair radicals, when the distances between the unpaired electrons are fairly large and the exchange integral $J$ is small, and not at the instant of direct contact between the radicals. However, in some cases the exchange interaction is presumably significant and this alters the process dynamics. In particular, such a situation can occur in biradical systems [49].

The nature of the influence of the exchange interaction on the $S-T$ transitions can be predicted fairly readily for the $\Delta g$ mechanism. Indeed, when no account is taken of the exchange interaction, the energy levels of the $S$ and $T_0$

states coincide, so that the transitions take place between two resonance levels. The exchange interaction splits the $S$ and $T_0$ levels, stops their resonance, and reduces the probability of the $S$ and $T$ transition [37].

In the HFI mechanism, the influence of the exchange interaction on the dependence of the $S-T$ mixing on the field is qualitatively different: the efficiency of the $S-T$ transitions passes through a maximum in the region of magnetic fields where the Zeeman splitting of the triplet levels is comparable to the singlet–triplet splitting and the singlet is in resonance with one of the triplet states, $T_{+1}$ or $T_{-1}$.

However, the exchange interaction ceases to play a role in singlet–triplet transitions if the lifetimes of the radical pairs in the "cage" are fairly short. Indeed, it can be shown that, for short-lived radical pairs, where $(\omega^2_{ST_0} + 4J^2)^{1/2}t < 1$, the probability of transition via the $\Delta g$ mechanism is independent of $J$ and coincides with the result defined by Eqn.(3) for $J = 0$. Similarly, in the case of the HFI mechanism of the singlet–triplet transition for short-lived radical pairs, where $(A^2_{\text{eff}} + J^2)^{1/2}t < 1$, the results defined by Eqns.(5) and (6) remain valid regardless of the exchange interactions.

Thus the dynamics of the radical pair spins are fully described in the case of the $\Delta g$ transition mechanism. For the HFI mechanism, calculations have been made of the dependence of the transitions of the radical pair on the magnetic field strength in the simplest systems, which made it possible to discover certain general characteristics over the singlet–triplet evolution of radical pairs. However, in the general case, a quantitative discussion of the effects due to the HFI mechanism, apparently requires calculations for each specific pair of radicals, since the transition probability depends significantly on the number of magnetic nuclei and the magnitude and signs of the HFI constants.

## IV. PHENOMENOLOGICAL MODELS OF THE RECOMBINATION OF RADICALS IN THE "CAGE"

Two models are considered for a phenomenological description of the recombination of radicals in the "cage": the diffusion [31] and exponential [25,29] models. According to the diffusion model, the "cage" for a radical pair consists of a region with a radius of approximately $10^{-7}$ cm and the lifetime of the radicals in the "cage" is determined by the time which they take to traverse this region. For solutions where the diffusion coefficient of radicals is $10^{-5}$ cm$^2$ s$^{-1}$, their lifetime in the "cage" is $10^{-9}-10^{-10}$ s.[31] This time can increase significantly, for example for highly viscous solutions. The recombination of radical pairs is treated phenomenologically. It is assumed that there is a reaction region, included between two concentric spheres with radii $r_0 - a$ and $r_0$, and that the recombination of singlet radical pairs in this region is characterised by a unimolecular constant $k(s^{-1})$.

Highly reactive radicals recombine on first contact with one another if the radical pair is in the singlet state. However, if the reactivity is not quite so high, repeated collisions of the radicals in the pair contribute to the overall recombination probability in addition to the first contact. Within the framework of the diffusion model, singlet–triplet transitions occur in the periods between collisions.

The statistics of repeated collisions in the "cage" have been examined in detail by Noyes [31]. On the basis of numerical calculations for repeated molecular collisions within the framework of "jumps" (the so-called random flight model), Noyes proposed the following approximation to the statistical weight $f(t)$ of the radicals in the "cage" involved in repeated encounters after a time $t$ when the initial distance between the pair radicals exceeds their collision radius by the distance of a single elementary jump [50]:

$$f(t)\,dt = \frac{0.24}{\tau}\,\frac{dt}{(t/\tau + 0.44)^{3/2}}, \qquad (7)$$

with $\tau$ as the average time of a single elementary jump, a typical value of which is $\tau \simeq 10^{-11}$ s.

The exponential model of recombination differs significantly in its physical postulates from the diffusion model. In this model, repeated collisions of the radicals are not taken into account and it is assumed that a singlet–triplet transition occurs directly in the reaction zone. The liberation of radicals from the "cage" is described as unimolecular decomposition of the pair with a Poisson distribution of the radical pair lifetimes:

$$f(t)\,dt = \frac{dt}{\tau_c}\exp\left(-\frac{t}{\tau_c}\right), \qquad (8)$$

where $\tau_C$ is the average lifetime of the radical pair in the "cage". The recombination of the radical pair in the singlet state competes with the process involving the liberation of the radicals from the "cage". The model described has been used in the theory of chemically induced nuclear polarisation [29] and in the theory of the triplet–triplet annihilation of electronically excited states in crystals [26].

The exponential model can describe adequately the kinetics of the recombination of radical pairs in the "cage" in a number of situations. When the solution contains a large number of radical traps, the probability of repeated contact between two given radicals becomes negligible and the "cage" recombination will correspond to the exponential model. The latter may be useful also when the radicals are held in the "cage" as a result of the formation of complexes or Coulombic attraction (in the recombination of radical-ions).

## V. APPROXIMATE CALCULATIONS OF THE EFFECT OF THE MAGNETIC FIELD IN RADICAL REACTIONS

For approximate estimates of the nature and scale of the field dependence of the probability of the recombination of radicals in the "cage" within the framework of the diffusion model, it is sufficient to restrict the treatment to a single repeated collision. It is then possible to calculate the probability of the $S-T$ transition averaged over the radical pair *ensemble*, using, for example, the distribution defined by Eqn.(7) with respect to the repeated collision times. Within the framework of the exponential model, one must find for such an estimate the probability of the $S-T$ transitions during the residence time of the radicals in the "cage", without taking into account recombination, averaged with the aid of the distribution defined by Eqn.(8). Presumably the efficiency of the recombination of the radical pair is proportional to the average population of the singlet state of the radical pair. The results of exact calculations confirm that this hypothesis is reasonable.

We shall now consider the results of estimates for an initial singlet pair. The following equations have been obtained for the probability of $S-T_0$ transitions induced by the $\Delta g$ mechanism: (a) within the framework of the exponential model [34]

$$\bar{p}_{ST_0}=\frac{1}{2}\frac{\omega^2_{ST_0}\tau_c^2}{1+\omega^2_{ST_0}\tau_c^2} \tag{9}$$

and (b) within the framework of the diffusion model[80]:

$$\bar{p}_{ST_0}=0.30\sqrt{\omega_{ST_0}\tau}. \tag{10}$$

We may note that the last result was obtained subject to the additional assumption that the quantity under the square root sign is small, which is true in most cases.

The typical differences between the $g$-factors of free radicals are $\Delta g \simeq 10^{-4}$–$10^{-3}$. Assuming that the lifetime of the radical pair in the "cage" is in the range $\tau_c \simeq 10^{-10}$–$10^{-9}$ s and that $\tau \simeq 10^{-11}$ s, we find that the $\Delta g$ mechanism should have a relatively weak influence on the probability of radical recombination in laboratory fields $H_0 \simeq 10^{-4}$ G. However, with increase of the viscosity by 1–2 orders of magnitude or for systems with a larger difference between the $g$-factors, the effects of the magnetic field may be considerable.

Table 2. The average probabilities of the $S-T$ transition in the radical pair for the diffusion model taking into account only one collision ($A\tau < 1$).

| No. of pair | $\overline{p^0_{ST}}$ | $\overline{p^\infty_{ST}}$ | No. of pair | $\overline{p^0_{ST}}$ | $\overline{p^\infty_{ST}}$ |
|---|---|---|---|---|---|
| I | $0.30\sqrt{A\tau}$ | $0.15\sqrt{A\tau}$ | IV | $0.34\sqrt{A\tau}$ | $0.20\sqrt{A\tau}$ |
| II | $0.24\sqrt{A\tau}$ | $0.15\sqrt{A\tau}$ | V | $0.22\sqrt{A\tau}$ | $0.21\sqrt{A\tau}$ |
| III | $0.30\sqrt{A\tau}$ | $0.15\sqrt{A\tau}$ | VI | $0.31\sqrt{A\tau}$ | $0.24\sqrt{A\tau}$ |

Note. The relation $\overline{p^0_{ST}} > \overline{p^\infty_{ST}}$ holds for all the radical pairs.

The results of calculations of the average probability of the $S-T$ transitions are summarised in Tables 2 and 3 for the HFI mechanism in the same systems for which Table 1 lists the solutions of the dynamic problems of the singlet–triplet evolution of the radical pair. The estimates which are based on the formulae quoted in Tables 2 and 3 for typical HFI parameters $A \simeq 10^8$–$10^9$ $s^{-1}$ and the parameters of the diffusion of radicals in solution $\tau_c \simeq 10^{-9}$ s and $\tau \simeq 10^{-11}$ s show that the probability of the $S-T$ transition changes by approximately 0.1 with increase of the magnetic field strength from zero to $H_0 \gg A$. There is a corresponding change in the probability of the recombination of radicals in the "cage". It follows from the data in Table 2 that the field effect depends on the specific structure of the radicals. The effect is small for radical pairs in which an anomalous time variation of the $S-T$ transitions is observed (for example, the radical pairs V and VI in Table 1). In this case, the contribution of the short- and long-lived radical pairs frequently cancel out on being averaged and the effect diminishes (Table 3).

For nuclei with a spin $I > \frac{1}{2}$, the probability of $S-T$ transitions has been calculated only in the case of radical pairs with a single magnetic nucleus [43,45]. Within the framework of the exponential model, the following results have been obtained for the initial singlet radical pair:

$$\bar{p}^0_{ST}=\frac{1}{2}\frac{I(I+1)A^2\tau_c^2}{1+\left(I+\frac{1}{2}\right)^2A^2\tau_c^2},$$
$$\bar{p}^\infty_{ST_0}=\frac{1}{2(2I+1)}\sum_{m=-I}^{I}\frac{A^2m^2\tau_c^2}{1+A^2m^2\tau_c^2}. \tag{11}$$

Eqns. (11) make it possible to treat the changes in the radical recombination probability following isotopic substitution.

Table 3. The average probabilities of the $S-T$ transition in the radical pair for the exponential model.

| No. of pair | $\overline{p^0_{ST}}$ | $\overline{p^\infty_{ST}}$ |
|---|---|---|
| I | $\frac{3}{8}\left\{\frac{A^2\tau_c^2}{1+4A^2\tau_c^2}+\frac{A^2\tau_c^2}{1+A^2\tau_c^2}\right\}$ | $\frac{1}{4}\frac{A^2\tau_c^2}{1+A^2\tau_c^2}$ |
| II | $\frac{3}{4}\frac{A^2\tau_c^2}{1+{}^9/_4A^2\tau_c^2}$ | $\frac{1}{4}\frac{A^2\tau_c^2}{1+A^2\tau_c^2}$ |
| III | $\frac{1}{4}\frac{A^2\tau_c^2}{1+{}^9/_4A^2\tau_c^2}+\frac{1}{2}\frac{A^2\tau_c^2}{1+3A^2\tau_c^2}$ | $\frac{1}{4}\frac{A^2\tau_c^2}{1+A^2\tau_c^2}$ |
| IV | $\frac{5}{6}\frac{A^2\tau_c^2}{1+{}^9/_4A^2\tau_c^2}+\frac{2}{3}\frac{A^2\tau_c^2}{1+9A^2\tau_c^2}$ | $\frac{1}{4}\frac{A^2\tau_c^2}{1+A^2\tau_c^2}+\frac{1}{4}\frac{A^2\tau_c^2}{1+4A^2\tau_c^2}$ |
| V* | $\frac{3}{8}\frac{A^2\tau_c^2}{1+A^2\tau_c^2}$ | $\frac{1}{8}\frac{A^2\tau_c^2}{1+{}^1/_4A^2\tau_c^2}$ |
| VI* | $\frac{15}{16}\frac{A^2\tau_c^2}{1+4A^2\tau_c^2}+\frac{3}{16}\frac{A^2\tau_c^2}{1+A^2\tau_c^2}$ | $\frac{9}{32}\frac{A^2\tau_c^2}{1+{}^9/_4A^2\tau_c^2}+\frac{3}{32}\frac{A^2\tau_c^2}{1+A^2\tau_c^2/4}$ |

Note. The relation between $\overline{p^0_{ST}}$ and $\overline{p^\infty_{ST}}$ for radical pairs Nos. V and VI depends on $A\tau_c$: $\overline{p^0_{ST}} > \overline{p^\infty_{ST}}$ when $A\tau_c \leqslant 1$ and $\overline{p^0_{ST}} < \overline{p^\infty_{ST}}$ when $A\tau_c > 1$; for the remaining pairs, $\overline{p^0_{ST}} > \overline{p^\infty_{ST}}$.

## VI. GENERALISATION OF THE THEORY OF THE DIFFUSION RECOMBINATION OF RADICAL PAIRS AND RADICALS IN HOMOGENEOUS SOLUTIONS

A more detailed description of the influence of the magnetic field on radical reactions and also a description of the effect of the polarisation of nuclear and electron spins during chemical reactions required a revision of the traditional theory of the recombination of radicals in solution taking into account singlet–triplet transitions. Such generalisation of the theory for the recombination of correlated radical pairs has been achieved [37,45,47,51,52]. The theory of the recombination of radicals in random encounters in space, which takes into account logically the spin selection rules in the reaction and the role of interactions removing the spin prohibition, has been formulated [38,45]. In the generalised theory, it is necessary to

take into account simultaneously the changes in the spin and spatial coordinates of the radicals. This can be done using the formalism of the density matrix[53]. It has been shown [37,45,47] that the density matrix $\rho(\boldsymbol{r},t)$ of the *sub-ensemble* of radical pairs where the radius-vector between the radicals assumes a value $r$ at time $t$ satisfies the equation

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t}=\hat{Q}_0\rho(\mathbf{r},t)-\frac{i}{\hbar}[\hat{V}(\mathbf{r}),\rho(\mathbf{r},t)]+D\Delta\rho(\mathbf{r},t), \tag{12}$$

where the first term on the right-hand side specifies the change in the pair spin density matrix without taking into account the interaction between the radicals, $\hat{V}$ represents the Hamiltonian for the interactoin between the unpaired electrons of the radical pair, and the last term describes the kinematic change in the pair density matrix owing to the mutual diffusion of the radicals.

In some studies[51,52], an additional term which takes into account the destruction of the radical pair as the result of recombination, was introduced into the right-hand side of Eqn.(12). Other workers [37,45,47] take into account the recombination reaction by introducing the appropriate conditions at the boundary of the reaction zone. The probability of the recombination of the radical pair is

$$p_{\text{rec}}=4\pi r_0^2 D\cdot Tr\int_0^\infty \mathrm{d}t\nabla\rho(\mathbf{r},t)|_{r=r_0}, \tag{13}$$

where $Tr$ indicates convolution with respect to the spin variables of the radical pair.

Specific calculations for radical pairs have been achieved hitherto only in terms of the $S-T_0$ approximation. If the initial distance between the radicals is $R_0$ for all radical pairs, then the field dependence of the recombination probability for the $\Delta g$ mechanism of the $S-T_0$ transition is described by the following relations[37]: (a) for a singlet precursor of the radical pair

$${}^{S}p_{\text{rec}}=\frac{r_0}{R_0}\frac{1}{1+q}\left[1+x+\cos\left(\frac{R_0-r_0}{r_0}x\right)\exp\left(-\frac{R_0-r_0}{r_0}x\right)\right]\Big/\left(2+\frac{1+2q}{1+q}x\right) \tag{14}$$

and (b) for a triplet precursor of the radical pair:

$${}^{T}p_{\text{rec}}=\frac{1}{3}\frac{r_0}{R_0}\frac{1}{1+q}\left[1+x-\cos\left(\frac{R_0-r_0}{r_0}x\right)\exp\left(-\frac{R_0-r_0}{r_0}x\right)\right]\Big/\left(2+\frac{1+2q}{1+q}x\right). \tag{15}$$

The following notation has been introduced in the above expressions:

$$q=D/kar_0,\quad x=(\omega_{ST_0}\tau_D)^{1/2},\quad \tau_D=r_0^2/2D. \tag{16}$$

The parameter $q$ defines the nature of the recombination: the rate of recombination is limited by the mutual diffusion of radicals for $q<1$ and by the reaction of radicals in the reaction zone (primary "cage") for $q>1$; $k$ is the rate constant for the recombination in a singlet pair ($s^{-1}$).

If the $S-T_0$ transitions are fairly rapid and there is sufficient time for their repeated occurrence during the lifetime of the radical pair in the "cage", then it follows from Eqns.(14) and (15) that the rate of recombination of the radical pair in the reaction zone is described by an average effective rate constant equal to $k/2$. The dependence of the recombination probability on field strength in moderate fields is described by equations which are qualitatively the same, as regards the nature of the dependence on $H_0$, as the approximate formulae obtained above taking into account only a single repeated encounter of the radicals. As an illustration, Fig. 3 presents the variation of the recombination probability of radical pairs with the magnetic field calculated from the formulae obtained by Salikhov et al.[37] The curves in Fig. 3 correspond to radical pairs which are initially located at the boundary of the reaction zone and correspond to different values of the parameter $\lambda$:

$$\lambda=\frac{k}{k+D/ar_0}. \tag{17}$$

Fig. 3 shows that the probability of the recombination of the initial singlet radical pair should fall with increase of the magnetic field and that of the triplet pair should increase.

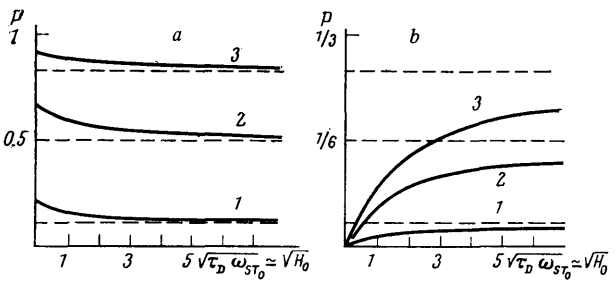



**Figure 3.** Variation with the magnetic field of the probability of the recombination of singlet (*a*) and triplet (*b*) radical pairs for the $\Delta g$ mechanisms of the $S-T$ transition corresponding to different values of $\lambda$: 1) 0.2; 2) 0.66; 3) 0.91.

The conditions for the observation of the field effect in the case of a triplet radical pair are particularly favourable, since in zero fields, where the $\Delta g$ mechanism is ineffective, the recombination product should be altogether absent.

In contrast to the recombination of correlated radical pairs, in the recombination of radicals in space one must consider the reaction of an *ensemble* of radicals randomly distributed in the system. The kinetic equations for the change in the spin density matrix for radicals A and B owing to their recombination reaction have been obtained[38,45] and are of the following form:

$$\left(\frac{\partial\rho^{\text{A}}}{\partial t}\right)_{\text{rec}}=-c_{\text{B}}(0)D\cdot Tr_{\text{B}}\int_{s(R)}\mathrm{d}s\Delta\rho^{\text{AB}}(r,t),$$

$$\left(\frac{\partial\rho^{\text{B}}}{\partial t}\right)_{\text{rec}}=-c_{\text{A}}(0)D\cdot Tr_{\text{A}}\int_{s(R)}\mathrm{d}s\Delta\rho^{\text{AB}}(r,t), \tag{18}$$

where $c_{\text{A}}(0)$ and $c_{\text{B}}(0)$ are the initial radical concentrations in solution. The right-hand sides of these equations describe the kinematic flux of the pair density matrix $\rho^{\text{AB}}$ from the "cage". Hence the solution of Eqns.(12) must be substituted as $\rho^{\text{AB}}$. However, in contrast to the recombination of radical pairs, for the reaction in a homogeneous solution with fairly long distances between the radicals, the following boundary condition must be adopted in conformity with the hypothesis that the correlation is weakened[54].

$$\rho^{\text{AB}}(r,t)\xrightarrow[r\to\infty]{}\rho^{\text{A}}(t)\times\rho^{\text{B}}(t). \tag{19}$$

Kinetic equations for the concentrations of radicals can be obtained from Eqn. (18) and (19) using the relations

$$c_{\text{A}}(t)=c_{\text{A}}(0)\cdot Tr\rho^{\text{A}}(t),\quad c_{\text{B}}(t)=c_{\text{B}}(0)\cdot Tr\rho^{\text{B}}(t). \tag{20}$$

The dependence of the recombination rate constant on the magnetic field has been analysed [38] with the aid of these equations in two cases: when the radicals have different $g$-factors and when one of the partners has a single magnetic nucleus with a spin of 1/2. For the $\Delta g$ mechanism, the recombination rate constant is

$$k_0 = 4\pi r_0 DF, \quad F = \frac{1}{2}\,\frac{1+x}{2(1+q)+(1+2q)x}. \tag{21}$$

Hence it follows that $k_0$ increases with the strength of the external magnetic field. This implies that the triplet radical pairs make the dominant contribution to the effect in random encounters. The influence of the magnetic field is particularly marked in diffusion-controlled reactions where $q < 1$. Fig. 4*a* presents the results of the calculation of the field dependence of the recombination efficiency in the encounter of two radicals for two values of $\lambda$.

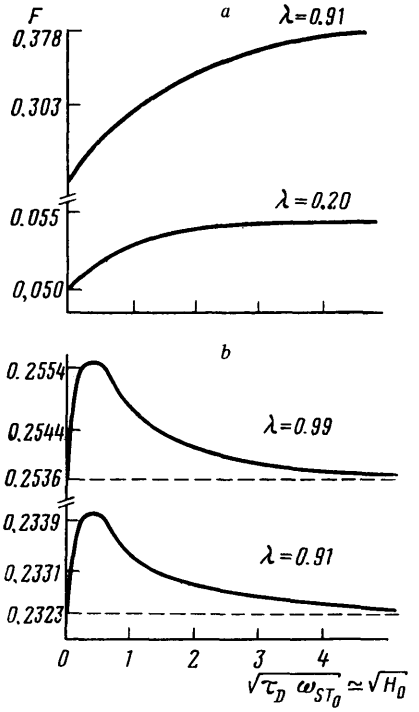



Figure 4. The efficiency of the recombination of radicals involved in random encounters in solution for the $\Delta g$ (*a*) and HFI ($A\tau = 0.01$) (*b*) mechanisms of the transitions in the radical pair in the "cage".

An interesting feature of the diffusion recombination of radicals in homogeneous solutions is that it reaches a steady state only for times of the order of the lifetime of the radical pair in the "cage" [55]. It has been shown [38] that singlet–triplet transitions increase the time taken by the reaction to attain kinetic conditions. For the $\Delta g$ mechanism, the rate of recombination tends to a steady-state value defined by Eqn. (21) in accordance with the law

$$k_0(t) = k_0\left(1 + \frac{r_0}{(\pi Dt)^{1/2}}\,2F\right). \tag{22}$$

Hence it follows that magnetic effects may be manifested also in the region where the recombination kinetics attain a steady state.

In $S$–$T$ transitions with a main HFI mechanism, exact relations for the field dependence of the rate constant have been so far obtained only when one of the radicals of the pair has a single magnetic nucleus with a spin of 1/2. [38] The results are illustrated in Fig. 4*b*, which demonstrates one of the unexpected but possible characteristics of the HFI mechanism: in fields $H_0$ comparable to the local field due to HFI there is a possibility of a maximum in the reaction efficiency. We may note that the changes in $F$ in regions of the maximum greatly exceed the difference between the values of $F$ in zero and strong magnetic fields. Presumably the appearance of the maximum is not obligatory for all radicals and should depend on their specific structure.

## VII. EQUATIONS DESCRIBING THE RECOMBINATION OF RADICALS WITHIN THE FRAMEWORK OF THE EXPONENTIAL MODEL

Bearing in mind that the exponential model of the recombination of radicals in solutions is widely used in the consideration of spin effects, we shall quote the corresponding kinetic equations. In the recombination of radical pairs, the pair density matrix satisfies the equation

$$\frac{\partial \rho^{AB}}{\partial t} = -\frac{i}{\hbar}[\hat{H}_{AB}, \rho^{AB}] - \frac{k}{2}(\hat{P}\rho^{AB} + \rho^{AB}\hat{P}) - \frac{1}{\tau_c}\rho^{AB}. \tag{23}$$

where the last term describes the liberation of the radicals from the "cage" and the penultimate term describes the destruction of the radical pair as a result of recombination; $\hat{P}$ is the projection operator onto the singlet state of the radical pair.

The kinetic equations describing the recombination of radicals in homogeneous solutions assume the following form [25,40,45]:

$$\left(\frac{\partial \rho^{A}}{\partial t}\right)_{rec} = -4\pi r_0 D \cdot c_B(0) \cdot T r_B(\rho^A \times \rho^B - \rho^{AB}),$$
$$\left(\frac{\partial \rho^{B}}{\partial t}\right)_{rec} = -4\pi r_0 D \cdot c_A(0)\, T r_A(\rho^A \times \rho^B - \rho^{AB}), \tag{24}$$

in which the pair matrix is found from the solution of the equation

$$\frac{\partial \rho^{AB}}{\partial t} = -\frac{i}{\hbar}[\hat{H}_{AB}, \rho^{AB}] - \frac{k}{2}(\hat{P}\rho^{AB} + \rho^{AB}\hat{P}) - \frac{1}{\tau_c}(\rho^{AB} - \rho^A \times \rho^B), \tag{25}$$

where, in contrast to Eqn. (23), account was taken also of the formation of the radical pair as a result of the random entry of two radicals into the "cage".

We may note that Eqns. (24) and (25) agree with the initial equations of the theory of the triplet–triplet annihilation of excitons in crystals [25] and of the quenching of excited triplet molecules in solutions [33]. We shall therefore return to these equations in the discussion of the quenching of the luminescence in solutions in the text below.

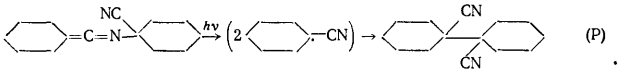
The solution of these equations show [40] that the exponential model yields qualitatively the same field dependence of the reaction efficiency as the diffusion model. Furthermore, exact calculations within the framework of the exponential model confirm the validity of the conclusions reached on the basis of approximate calculations.

## VIII. SPIN EFFECTS IN RADICAL REACTIONS

The models enumerated above for the description of the influence of the magnetic field on radical reactions are based on the hypothesis that spin effects play an important role in such reactions. We shall consider the experimental evidence for the manifestation of spin prohibitions in the recombination reactions of free radicals.

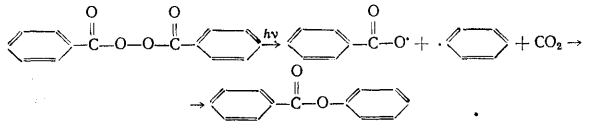
We shall consider in the first place the recombination of correlated radical pairs in the "cage", where the recombination efficiency may be expected to depend on the spin multiplicity of the radical pair (in the absence of mechanisms of rapid transitions between different spin states).

The influence of the spin multiplicity of radical pairs has been taken into account in a number of studies where direct and sensitised photolytic reactions were compared. Thus Fox and Hammond[56] observed an appreciable difference between the yields of the products of the recombination of two cyanocyclohexyl radicals in the photolysis of *N*-(1-cyanocyclohexyl)pentamethylene ketenimine:



(P)

In direct photolysis (via an excited singlet state) in carbon tetrachloride, approximately 24% of succinonitrile (P) is formed. The triplet-sensitised decomposition under the same conditions gives only 8% of compound (P). Thus the probability of the recombination of singlet radical pairs is in this case three times greater than that of the triplet pairs. Similar effects have been observed in the direct and sensitised photolysis of benzoyl peroxide[57]:




The yield of phenyl benzoate was approximately 3% for the triplet radical pairs and approximately 8% for the singlet pairs.

The effects of the spin multiplicity of the sensitiser on the formation of phenyl benzoate have been investigated recently for the same system[58]. Benzoyl peroxide solutions in toluene or benzene were irradiated by light from a high-pressure mercury lamp in the presence of aromatic hydrocarbons (naphthalene, fluorene, phenanthrene, etc.), which are singlet sensitisers, and also of aromatic ketones—acetophenone, benzophenone, and 2-methylbenzophenone. The latter are typical triplet sensitisers. It has been shown that the yield of phenyl benzoate is $\leqslant 3.0\%$ in the presence of triplet sensitisers and $\geqslant 10\%$ in the presence of singlet sensitisers.

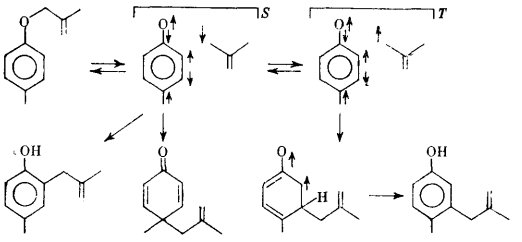
Another class of reactions in which spin prohibition may be manifested includes the recombination of radicals in space. When two radicals react in each collision, the rate of their recombination will be determined solely by the rate of diffusion. The rate constant for such a diffusion-controlled reaction is defined by the expression

$$k_D = \left(\frac{4\pi N}{1000}\right)(\sigma_A + \sigma_B)(D_A + D_B), \qquad (26)$$

where $N$ is the Avogadro number, $D_A$ and $D_B$ are the diffusion coefficients of the radicals A and B in the reaction medium, and $\sigma_A$ and $\sigma_B$ are their reaction radii.

However, one should bear in mind that two radicals recombine in the collision only when the radical pair formed as a result of their encounter is in the singlet state. Since the probability of singlet encounters is 1/4, presumably the measured values of $k_D$ should be smaller by a factor of 4 than those predicted by Eqn.(26). Analysis of the experimental results for the kinetics of the recombination of organic radicals does indeed show this relation. The values of $k_D$ calculated by Eqn.(26) for the most typical experimental conditions are approximately $8 \times 10^9$ litre mole$^{-1}$ s$^{-1}$.[59] On the other hand, the measured constants for bimolecular radical reactions do not as a rule exceed $2 \times 10^9$ litre mole$^{-1}$ s$^{-1}$.[59]

The above behaviour does not apparently obtain in reactions involving hydrogen atoms, H, OH and $HO_2$ radicals, and solvated electrons [60]. They are of interest for the process under consideration, because they are not sterically hindered and have zero activation energy. However, it has been found that the experimental values of $k_D$ for these reactions are close to those calculated by Eqn.(26). The causes of the apparent absence of spin prohibition in reactions of this class have been examined[60]. The very interesting possibility of the influence of the electron spin on the orientation effect in radical reactions is discussed in another investigation[61]. In the Claisen photochemical rearrangement (the photolysis of allyl *p*-methylphenyl ether), the authors observed the formation of the product of the substitution of the allyl group not only in the *ortho*- and *para*-positions but also in the *meta*-position in the aromatic ring. In the analogous thermal rearrangement, *meta*-products are not formed. The possibility of the formation of *meta*-products in the photochemical rearrangement can be understood by examining the following mechanism proposed on the basis of the analysis of the effects of chemically induced nuclear polarisation in this reaction:




The radical pairs formed in the singlet state yield mainly *ortho*- and *para*-substitution products. For triplet pairs, *ortho*- and *para*-substitution is spin-prohibited. However, the spin density is negative in the *meta*-position, so that addition of the allyl radical in this position can occur in the triplet radical. According to the authors, this in fact explains the formation of the *meta*-product.

The above examples show that the electron spin effects have in many instances a very marked influence on the kinetics of the recombination of free radicals. Consequently, when the rates of radical reactions are considered, account must be taken of electron spin prohibitions.

We shall now consider the effects of nuclear spin in radical recombination reactions. It follows from the above theoretical analysis that the hyperfine interaction of nuclei with electrons in the radical pair can lead to a singlet–triplet transition, i.e. to a change of the multiplicity of the radical pair. Since the HFI energies are different for different nuclear isotopes, one may expect differences between the recombination efficiencies of the radical pairs containing these isotopes. We shall call this phenomenon the magnetic isotope effect, in contrast to the usual kinetic isotope effect[34,37].

Experimental studies on isotope effects in radical reactions have been comparatively few and are practically all concerned with the rate of decomposition of organic peroxides and azo-compounds (see, for example, Seltzer and Hamilton [62] and Rummel et al. [63]). In many cases, anomalously large secondary isotope effects were observed in the thermal analysis of hydrogen- and deuterium-containing compounds ($k_H/k_D \simeq 1.3$–$1.4$) [63] which it would be tempting to interpret in terms of the difference between the magnetic properties of hydrogen and deuterium. The HFI constants for H and D are indeed known to differ by a factor of approximately 7. Consequently there is a greater probability of a change in the spin state (from $S$ to $T$) in hydrogen-containing radical pairs and thus one may expect that the efficiency of the reverse recombination of the primary pair, with reformation of the initial compound, will be smaller than for the deuterium analogue.

Unfortunately, in all these cases one cannot rule out the possibility that the isotope effect arises in the primary decomposition of the molecule and not in the reactions of the radical pair. There is then a possibility of an alternative explanation of the nature of the observed isotope effects, associated with the differences between the zero-point vibrational energies [64]. We shall only mention that a quantitative interpretation of the secondary isotope effects within the framework of these ideas involves considerable difficulties. We are familiar with only one study where a direct isotope effect on the rate of recombination of the radical pair was observed [65]. We shall consider it in greater detail. A study was made of the thermal decomposition of azobisisobutyronitrile (AIBN) and [12-D]AIBN in chlorobenzene at 65°C. The decomposition mechanism can be represented in the following form:

$$R{-}N_2{-}R \xrightarrow{k_I} (2R^{\cdot}) + N_2 \quad ,$$

$$(2R^{\cdot}) \xrightarrow{k_{II}} \text{recombination},$$

$$(2R^{\cdot}) \xrightarrow{k_{III}} 2R^{\cdot}\ \text{(diffusion)},$$

$$\dot{R}{=}N{\equiv}C{-}\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C^{\cdot}}}}} \quad ,$$

where round brackets represent the cage. The cage effect in this system has been studied in a large number of investigations and is well known. The authors were able to measure the quantity $a = k_{III}/(k_{II} + k_{III})$ which is inversely proportional to the efficiency of the recombination within the cage. It was found that $a_H = 0.56 \pm 0.015$ and $a_D = 0.51 \pm 0.015$. Since the radical recombination reaction ($k_{II}$) has virtually zero activation energy, the usual kinetic isotope effect is impossible. The observed difference between $a_H$ and $a_D$ has been attributed [65] to the influence of the mass of the radicals on their diffusion from the "cage". According to the authors, the probability of the diffusion of heavy radicals (with D) is lower, so that $a_D < a_H$. However, this explanation conflicts with the accepted theory of radical recombination in the "cage" [66]. According to Koenig and Fischer [66], the opposite effect should be observed—heavier radicals should give rise to a smaller yield of the recombination product (i.e. $a_D > a_H$).

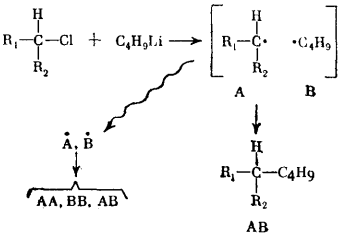
The observed effect can be simply explained on the basis of the different magnetic properties of the isotopes. In this case, it is possible to estimate quantitatively the expected magnitude of the isotope effect.

According to Eqn. (4), the effective HFI constants for radical pairs are $4 \times 10^8$ and $10^9$ rad $s^{-1}$ for [12-D]AIBN and [12-H]AIBN respectively. On substituting these values in the theoretical expression for the radical pair recombination probability (see Table 2, RP I), we find that the calculated isotope effect on the radical recombination efficiency (approximately 10%) agrees well with the observed value.

The above discussion shows that the possibility of the manifestation of "magnetic" effects must be borne in mind in the analysis of the nature of the experimental kinetic isotope effects in radical recombination reactions.

## IX. EXPERIMENTAL DATA FOR THE INFLUENCE OF THE MAGNETIC FIELD ON RADICAL REACTIONS

A number of studies, where the influence of the magnetic field on the rate of radical reactions was considered, have now been made. Some [41,42,47,48,67–69] were devoted to the reactions of alkyl-lithium with arylchloromethanes in solutions. The observation and analysis of the effects of the chemically induced polarisation of $^1H$, $^{19}F$, and $^{13}C$ nuclei showed that these reactions proceed via the following radical mechanism:




Thus the initial pair of two alkyl radicals in the singlet state is the direct precursor of the final product.

It has been observed [42] that, following an increase of the magnetic field from the terrestrial field (approximately 0.5 G) to $H = 20\,000$ G, the ratio of the main products AB and AA changes appreciably in the reaction of pentafluorobenzyl chloride ($R_1 = C_6F_5$ and $R_2 = H$) with butyl-lithium in boiling hexane. In a high magnetic field, [AB]/[AA] increases by 30%. It is readily seen that the observed effect is in good qualitative agreement with the HFI mechanism of the influence of the magnetic field discussed above. Indeed, in a strong field the probability of the $S$–$T$ transition in the pair of pentafluorobenzyl and butyl radicals diminishes, which entails an increase in the probability of the radical recombination within the cage. The latter leads in its turn to an increase of [AB]/[AA] with increasing magnetic field strength.

The study of the overall variation of [AB]/[AA] with field strength for this reaction [48] confirmed that the observed effect is due to the HFI mechanism. Fig. 5 illustrates the experimental variation of the ratio of the products AB and AA with the magnetic field strength for the reaction of pentafluorobenzyl chloride with butyl-lithium. The curve is S-shaped with a transitional region corresponding to $H \simeq 50$–$200$ G. Approximate calculations for the HFI model predict precisely this type of dependence of the population of the singlet state $p_S$ and the corresponding probability of the recombination of the singlet radical pairs on the magnetic field [48]. Fig. 6 illustrates the variation of $p_S$ with the magnetic field strength for several values of the HFI constant for a model radical pair with a single proton, calculated within the framework of the exponential model. Fig. 6 (curve *1*) shows that $p_S$ for radical pairs with $At < 1$ increases with increasing magnetic field and that the transitional region corresponds to

$H \simeq A/\gamma$. In the system investigated, the radical pair contains several magnetic nuclei and an appreciable change in $p_S$ should be observed in fields $H \simeq A_{eff}/\gamma = \frac{1}{\gamma}(\sum_i A_i^2)^{1/2} \simeq$ 60 G. Thus theoretical estimates within the framework of the HFI model agree satisfactorily with experiment.

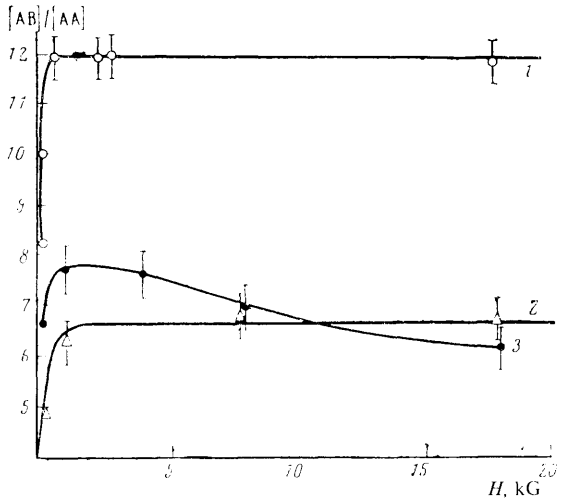



Figure 5. Experimental variation of the ratio of the reaction products AB and AA with the magnetic field strength in the reaction of $C_4H_9Li$ with pentafluorobenzyl chloride (curve *1*), *p*-fluorobenzyl chloride (curve *2*), and chlorodi-(pentafluorophenyl)methane (curve *3*).

It has been shown [69] that the influence of the magnetic field can also be observed in reactions of butyl-lithium with a series of other arylchloromethanes $\begin{matrix} R_1 \\ \diagdown \\ \\ \diagup \\ R_2 \end{matrix}$ CHCl, where $R_1 = C_6H_5$ and $R_2 = H$ (1), $R_1 = C_6H_4F$ and $R_2 = H$ (2), and $R_1 = R_2 = C_6F_5$ (3). The field dependence of [AB]/[AA] for compound (2) is of the same form as for the reaction of pentafluorobenzyl chloride with butyl-lithium (Fig. 5). Consequently, the magnetic field effects in this system are described by the HFI mechanism. On the other hand, in the reaction of chlorodi(pentafluorophenyl)methane in strong fields, an appreciable decrease of [AB]/[AA] is observed instead of a plateau (Fig. 5). The increase of [AB]/[AA] in fields ranging from 0.5 to 1000 G for chlorodi(pentafluorophenyl)methane is described satisfactorily by the HFI mechanism. The decrease of this ratio on further increase of $H$ has been explained [68,69] by the difference between the Zeeman energies of the electrons in the radical pair ($g_1\beta H - g_2\beta H$), which provides an additional mechanism of the singlet–triplet transition (the $\Delta g$ mechanism) and leads to a decrease in the probability of the radical recombination within the cage. A study of the effects of the chemically induced polarisation of the $^1H$ and $^{19}F$ nuclei did indeed demonstrate an appreciable difference between the *g*-factors of the di(pentafluorophenyl)methyl and butyl radicals [70]. The field dependence of the population of the singlet states of the radical pair has been calculated [68] within the framework of the exponential model with a simultaneous examination of the HFI and $\Delta g$ mechanisms of the $S$–$T$ transition in a radical pair with the same magnetic nucleus With a suitable choice of parameters, the calculated curve agrees satisfactorily with experimental curve (cf. Figs. 5 and 6).

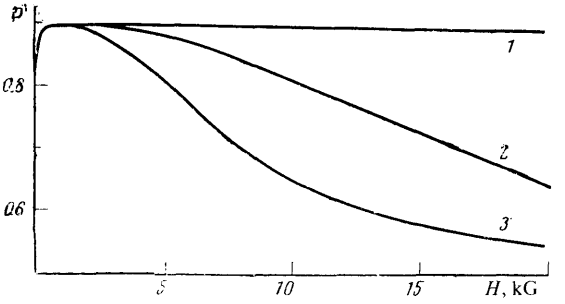



Figure 6. Calculated variation of the population of the singlet state of the radical pair having a single magnetic nucleus with the external magnetic field: *S* precursor; $\tau_c = 10^{-9}$ s; $A = 10^9$ rad $s^{-1}$; $\Delta g$: 1) 0; 2) 0.005; 3) 0.01.

The parameters specified in theoretical models to which the observed influence of the magnetic field corresponds have been discussed [48]. Using the experimental values $\{[AB]/[AA]\}_\infty = 12.2$ and $\{[AB]/[AA]\}_0 = 8.5$ for the reaction of pentafluorobenzyl chloride with $C_4H_9Li$ within the framework of the diffusion model of the radical pair for $A_{eff} = 10^9$ rad $s^{-1}$, $\tau = 6 \times 10^{-10}$ s was obtained as the time of the diffusion jump. This value exceeds appreciably the typical diffusion jump times ($10^{-11}$ s) for solvents with the usual viscosities. In order to account for this discrepancy, the authors [48] used the hypothesis [71] according to which the radicals in the system investigated are not involved in the reactions in a free state but in the form of a complex with an associated species of the organolithium compound. It is reasonable to expect that the characteristic diffusion time of such a conglomerate will be much longer than for a typical radical pair (approximately $10^{-11}$ s).

Thus one may conclude that, in order to obtain appreciable effects of the magnetic field on radical reactions (tens per cent), it is necessary to investigate reactions where the intermediate free radicals exhibit an anomalously low mobility ($10^{-9}$–$10^{-10}$ s). One of the ways of reducing diffusional mobility is to carry out the reactions in viscous solvents. It has been shown [42] for the above reaction of pentafluorobenzyl chloride with $C_4H_9Li$ that an increase of the viscosity of the solvent on passing from hexane to cyclohexane does indeed increase the magnetic effect. In the usual instances of radical reactions in solvents with normal viscosities ($\tau \simeq 10^{-11}$ s), insignificant magnetic effects are to be expected ($\lesssim 10\%$), these may not be susceptible to detection by the existing analytical methods. Analysis of the literature shows that all the published examples where the absence of an effect of the magnetic field on radical reactions in solvents has been demonstrated [18,19,72] can be included in precisely this class.

An interesting observation of the effects of the magnetic field has been made in a study [73] of the recombination of a pair of negative and positive radical ions. The idea of

the experiment was as follows. The solvent (squalane) molecule was ionised by pulse irradiation with fast electrons. Fluorene molecules, present in solution at a low concentration, capture both the electron and the parent positive ion. This results in the formation of a singlet pair of radical-ions linked by Coulombic forces and inevitably recombining. Before recombination, the radical pair may undergo the $S-T$ transition. The formation and recombination of the radical-ions can be represented schematically as follows:

$$S \rightsquigarrow S^+ + e^- , \quad (27)$$

$$S^+ + M \longrightarrow S + M^+ , \quad (28)$$

$$e^- + M \longrightarrow M^- , \quad (29)$$

$$M^+ + M^- \longrightarrow M^* + M . \quad (30)$$

Here S is the solvent (squalane), M the fluorene molecule, and M* the excited singlet and triplet states of fluorene. Presumably, as in the recombination of neutral free radicals, the magnetic field can influence the rate of the $S-T$ transition and hence the ratio of the excited singlet and triplet molecules.

An important experimental advantage in the study of this process has been the fact that the product of the recombination of the radical-ions is a molecule in an electronically excited state. The existing optical methods make it possible to determine with a high accuracy the concentrations of both singlet (from the fluorescence) and triplet (from the absorption) states. It is noteworthy that, in contrast to the radical reactions discussed above, the radical-ions formed in the pair cannot emerge from the "cage" and recombine with a probability of unity, since the initial distance between the charges (50–150 Å) is smaller than the Onsager radius for the solvent investigated (300 Å).

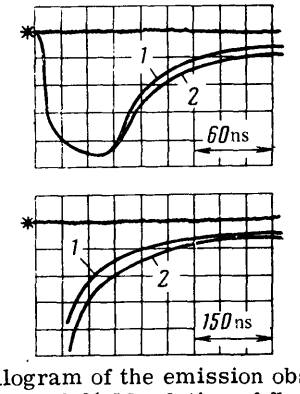



Figure 7. Oscillogram of the emission observed in the pulse radiolysis of a 0.01 M solution of fluorene in squalane in a 3 M eV electron accelerator[73]: 1) without a magnetic field; 2) in a 1000 G magnetic field.

Fig. 7 presents the oscillogram of the emission spectrum observed in the pulse radiolysis of a 0.01 M solution of fluorene in squalane using an electron accelerator with an energy of 3 M eV. Evidently, in a magnetic field ($H$ = 1000 G) the emission intensity after the pulse (approximately 50 ns) is appreciably higher. The observed effect implies that the population of the precursor singlet radical-ion pairs increases in the magnetic field, which can be explained qualitatively within the framework of the HFI model. A study[73] of the field dependence of the fluorescence intensity confirmed this conclusion. Fig. 8 shows that the overall form of the experimental curve is analogous to that calculated for the HFI mechanism (cf. Fig. 6). Since the yield of the singlet states increases in the magnetic field, one may expect a simultaneous decrease in the yield of the excited triplet states. Although in the latter case the situation is greatly complicated owing to the longer lifetime of the triplet states, the authors[73] nevertheless succeeded in observing experimentally a slight decrease of the concentration of triplets in the magnetic field (Fig. 8). It is noteworthy that, in control experiments with an anion, where the mechanisms of the magnetic effects discussed above do not operate, the magnetic field has almost no influence on the yield.

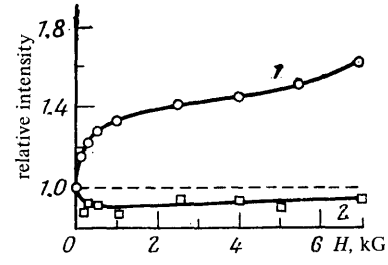



Figure 8. The influence of the constant magnetic field on the intensity of fluorescence (curve *1*) and absorption (curve *2*) in the pulse radiolysis of fluorene solutions in squalane[73]. The fluorescence and absorption were observed at 100 ns intervals after the pulse.

Analogous experiments designed to investigate the magnetic effects on the recombination of fluorene radical-ions in solutions have been carried out using a source of $\gamma$-radiation. The results of the measurements of the fluorescence intensity on radiolysis in different magnetic fields are illustrated in Fig. 9. It is noteworthy that, in contrast to the earlier investigation[73], here a study was made of the recombination of radical-ions in solvents of different viscosities. For the most viscous solvent (squalane), the effect of the magnetic field on the fluorescence yield and hence on the population of the singlet radical pairs is a maximum. In benzene, which had the lowest viscosity, the field effect could not be observed at all, while an intermediate situation was noted for cyclohexane. These results as well as those discussed above[42] confirm the theoretical conclusion that an increase of solvent viscosity can increase significantly the effect of the magnetic field in the recombination of the radical pair.

In conclusion, we shall consider the possibility of an effect by the magnetic field on radical reactions in solids. In this case, the decrease of diffusional mobility should in general favour the magnetic effects within the framework

of the mechanisms considered, with participation of radical pairs. So far there have been no reports in the literature of experimental observations of such effects.

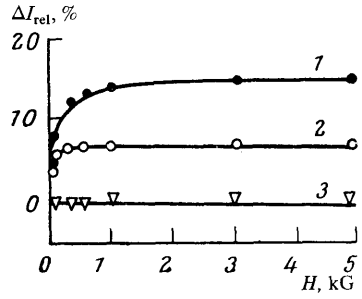



Figure 9. The influence of the magnetic field on the fluorescence intensity ($\Delta I_{rel}$ is the increase of the intensity) in the $\gamma$-radiolysis of fluorene solutions in different solvents: 1) squalane; 2) cyclohexane; 3) benzene[74].

The influence of the magnetic field on the concentration of free radicals in the low-temperature photolysis of formaldehyde has been investigated[75] by ESR. The system is of interest because the pair formed as a result of the photolysis

$$H_2CO \xrightarrow{h\nu} H\dot{C}O + \dot{H}$$

contain radicals with very high HFI constants: atomic hydrogen with $A$ = 500 g and the formyl radical with $A$ = 132 G. Only the formyl radical is detected in the ESR spectrum at 77 K, while the H atom is insufficiently stable under these conditions. The kinetics of the accumulation of HĊO radicals were studied in magnetic fields of 75 and 6200 G directly in the cavity of the ESR spectrometer (the residual magnetic field was 75 G). The experiments showed that the steady-state concentration of formyl radicals is higher in the photolysis in a high field (Fig. 10). The most important mechanisms of the destruction of HĊO radicals, leading to the establishment of a steady-state concentration, are associated with the following reactions:

$$H\dot{C}O \rightarrow \dot{H} + CO, \quad (31)$$

$$\dot{H} + H\dot{C}O \rightarrow H_2CO, \quad (32)$$

$$\dot{H} + H\dot{C}O \rightarrow H_2 + CO. \quad (33)$$

It has been suggested[75] that the magnetic field influences the recombination of a formyl radical and a hydrogen atom in a random encounter within the matrix [reactions (32) and (33)]. Indeed the sign of the effect corresponds qualitatively to the HFI mechanism of the influence of the magnetic field on $F$ pairs.

Analogous experiments, carried out with deuteroformaldehyde[75], failed to show an appreciable effect of the magnetic field on the steady-state light-induced concentration of DĊO radicals. According to the authors, this may be associated both with the lower HFI constants for the D atoms and DĊO radicals compared with Ḣ and HĊO and with the reduced mobility of atomic deuterium.

The effects of the magnetic field on the radiation-induced polymerisation of methyl methacrylate and acetaldehyde have been investigated at low temperatures[76,77] and it was found that the magnetic field influences both the rate of polymerisation and the molecular weight of the polymers formed. Since these processes can proceed via a free-radical mechanism, presumably the mechanisms of the influence of the magnetic field on the radical pair reactions examined above operate in these cases too. Both chain initiation and quadratic chain termination are magnetically sensitive stages of radical polymerisation.

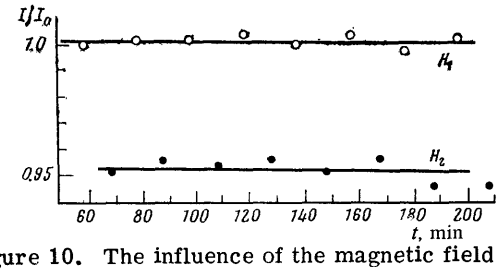



Figure 10. The influence of the magnetic field on the steady-state photochemically induced concentration of formyl radicals in the low-temperature photolysis of formaldehyde at 77 K ($H_1 > H_2$).[75]

In conclusion of this section, we may quote that the influence of the magnetic field on radical reactions is now fairly well understood. At the same time, it is clear that the regions where the expected effects should be maximum are so far not susceptible to experiment. This involves in the first place carrying out the reactions under conditions where the diffusional mobility of the radicals is lower by 1–2 orders of magnitude than the usual mobility and, in the second place, the study of the products of the triplet radical pairs within the "cage", where the effect of the relative change in the rate of reactions should be particularly pronounced.

## X. PROCESSES INVOLVING TRIPLET MOLECULES

Like free radical reactions, processes involving triplet molecules can be selective with respect to spin and can depend for this reason on the external magnetic field. As already mentioned in the introduction, such dependence was observed for the first time in solid organic crystals[23–26]. These studies stimulated analogous research on liquids. Spin-selective processes, which have been investigated experimentally in liquids and for which an effect of the magnetic field has been observed, are listed below.

1. The quenching of the excited triplet state by a free radical[78,79]. This process has a doublet final state and the quenching step can therefore occur only in collisions where the triplet molecule and the radical are in a collective doublet state.

2. Triplet–triplet annihilation[80]. In a random encounter in solution, a pair of triplet molecules can form singlet, triplet, and quintet states with respect to the total spin. Quenching takes place in the singlet state, since it leads to the formation of molecules in ground and excited singlet states.

3. The quenching of excited triplet states by oxygen [81]. Since oxygen has a triplet ground state, this process is analogous to the triplet–triplet annihilation and is also spin-selective.

4. The photochemical oxidation of aromatic hydrocarbons [82]. The primary stage in this reaction is the formation of an excited singlet oxygen molecule as a result of the collision of an excited triplet hydrocarbon molecule with oxygen in the ground state. The influence of the magnetic field on this process has so far been established only for the reaction in the solid phase.

The influence of the magnetic field on the above processes is interpreted in terms of a mechanism formally identical with that examined for the recombination reactions of free radicals. According to the dominant view, the magnetic field influences the dynamics of the spins of two paramagnetic species, i.e. the rate of change of the multiplicity of the pair of paramagnetic species which have collided in solution. The change in multiplicity can occur both on direct contact of the species and during their lifetime in the "cage", during the intervals between repeated collisions of a given pair of paramagnetic species.

As in the recombination of radicals, the change in spin multiplicity can again be induced by the $\Delta g$ and HFI mechanism. However, the transitions due to the dipole–dipole interaction of the unpaired electrons of each of the triplet molecules are more effective for the latter. In solutions, the thermal motion of triplet molecules modulates this dipole–dipole interaction in a random fashion, which leads to an effective paramagnetic relaxation of the triplet molecules. These relaxation transitions mix the states of two paramagnetic species with different multiplicities. Thus the influence of the magnetic field on elementary processes involving triplet molecules in solutions is interpreted as the result of the field dependence of the relaxation transitions caused by the fluctuating dipole–dipole interaction in the triplet molecules. We point out yet again that this interpretation is quite equivalent to the mechanism proposed by Brocklehurst [32] to account for the effect of the magnetic field in radiation-chemical reactions.

The influence of the magnetic field on processes involving triplet molecules in solutions has been examined theoretically by Atkins and Evans [33], who investigated comparatively non-viscous solutions where the molecular rotation is fairly rapid so that stochastic perturbation theory and the Redfield equation can be used to calculate the kinetic coefficients describing the relaxation transitions [33]. A theory of the processes under consideration may be developed on the basis of the fundamental equations which were quoted above in the discussion of the radical recombination reaction [Eqns. (12)–(25)]. The specific features of a real system are reflected in the formulation of the equations for the pair density matrix $\rho AB$.

Atkins and Evans calculated the probability of the triplet–triplet annihilation in arbitrary magnetic fields. The following expression has been obtained for the ratio of the intensities of the fluorescence accompanying this annihilation in strong (approximately 10 000 G) and zero magnetic fields:

$$I_H/I_0 = 1 - 0.61\Phi_{TT}(k(0)\tau_a)^{1/2}, \quad (34)$$

where $\tau_a$ is the duration of the elementary step in translational diffusion, $\Phi_{TT}$ is related to the probability $\lambda_T$, that the triplets which have collided will be annihilated subject to the condition that the pair was in the singlet state during the encounter, by the expression

$$\Phi_{TT} = \lambda_T/(1-\lambda_T); \quad (35)$$

and $k(0)$ is the spectral density of the dipole–dipole interaction at zero frequency:

$$k(0) = (D^2 + 3E^2)\tau_r. \quad (36)$$

Here $D$ and $E$ are the principal values of the dipole–dipole interaction tensor and $\tau_r$ is the characteristic rotational relaxation time.

Analogous reasoning for the quenching of triplet molecules by radicals leads to the following results [33]:

$$I_H/I_0 = 1 + 0.95\Phi_{DT}(k(0)\tau_a)^{1/2}, \quad (37)$$

where $\Phi_{DT}$ is related to the probability of the quenching of the triplet $\lambda_D$ in such a collision, where the pair was in the doublet state, by the expression

$$\Phi_{DT} = \lambda_D^2/\left(1 - \frac{4}{3}\lambda_D + \lambda_D^2\right). \quad (38)$$

Theoretical analysis shows that the probabilities of the triplet–triplet annihilation and of the quenching of the triplet biradicals in solutions should decrease with increasing magnetic field strength. The opposite variation with the field should be observed for the fluorescence intensity in such a case. The theory predicts in addition that the transitional region is located in fields corresponding to the equality of the Zeeman and rotational frequencies.

The theoretical results [33] are in good qualitative and quantitative agreement with numerous experiments [80–90]. Tables 4–6 list systems in which the magnetic field has an effect on the elementary processes involving triplet molecules.

Table 4. Experimental results for the influence of the magnetic field on the rate of triplet–triplet annihilation in solutions (for delayed fluorescence).

| Reaction | Change in luminescence intensity, % (for H = 8 kG)** | References |
|---|---|---|
| $T + T \rightarrow S + S_0$ | | |
| $(\text{Anthracene})^T + (\text{Anthracene})^T$ | | |
| in dimethylformamide | 4–5 | 80 |
| in acetonitrile | 2 | 81 |
| $(\text{Pyrene})^T + (\text{Pyrene})^T$ | | |
| in dimethylformamide | 2–3 | 81 |
| in acetonitrile | 1–2 | 81 |
| in cyclohexane | 6–7 | 84 |
| $(\text{1,2-Benzanthracene})^T + (\text{1,2-Benzanthracene})^T$ | | |
| in cyclohexane | 4 | 84 |
| $(\text{Anthracene})^T + (\text{Anthracene})^T$ in $CH_2Cl_2$ | 5 | 85 |
| $T + T \rightarrow E^* + S_0$ | | |
| $(\text{Pyrene})^T + (\text{Pyrene})^T$ | | |
| in cyclohexane | 6–7 | 84 |
| $(\text{1,2-Benzanthracene})^T + (\text{1,2-Benzanthracene})^T$ | | |
| in cyclohexane | 3 | 84 |

*E = excimer.

**In the magnetic field, the luminescence intensity diminishes, indicating a decrease in reaction rate.

The first successful observation of the influence of the magnetic field was made in 1969 by Faulkner and Bard in a study of the delayed fluorescence of anthracene in solution on photoexcitation [80]. Delayed fluorescence (DF) is known to arise as a result of the formation of an excited singlet state on annihilation of two triplet states: $T + T \rightarrow$

$S + S_0$ ($T$ and $S$ are the excited triplet and singlet states and $S_0$ is the ground state of the molecule). The DF intensity is then defined by the expression

$$I_{DF} = \frac{1}{2}\Phi_f k_a (I_a \Phi_T \tau)^2, \quad (39)$$

where $\Phi_f$ is the probability of fluorescence, $k_a$ the rate constant for the triplet–triplet annihilation, $I_a$ the rate of absorption of light, $\Phi_T$ the probability of the formation of the triplet state, and $\tau$ the lifetime of the triplet state.

It has been observed [80] that the DF intensity decreases with increase of the magnetic field strength (see Fig. 11 and Table 4). In principle, both $\Phi_T$ and $k_a$ are magnetically sensitive quantities. Experiments on sensitised photolysis permitted a more unambiguous solution of this problem. Whereas in direct photolysis the triplet states of anthracene arise as a result of an intercombination transition from excited singlet states, on sensitisation they are populated in a triplet–triplet energy transfer process. Consequently, in such cases the efficiency of the formation of triplet states $\Phi_T$ is determined by different processes. It has been shown [80] that the variation of the DF intensity with the magnetic field is the same for both direct and sensitised photolysis. This enabled the authors [80] to conclude that the observed variation of the DF intensity in the magnetic field is due to the influence of the latter on the triplet–triplet annihilation rate constant. The decrease of the rate of the triplet–triplet annihilation in the magnetic field (to 7%), manifested in the DF spectra, was subsequently observed also for a number of other systems (see Table 4). It is noteworthy that the effect of the magnetic field depends strongly on the solvent, which apparently indicates a significant role of the medium in the annihilation processes. In a study of DF in pyrene and 1,2-benzanthracene solutions [84], it was possible to observe the influence of the magnetic field not only on the fluorescence of the monomeric molecules but also on that of dimers (exciplexes).

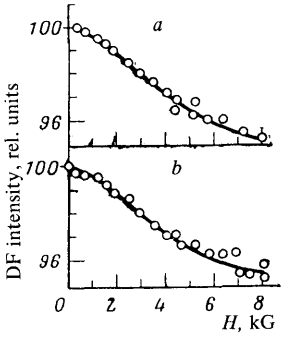



**Figure 11.** The effect of the magnetic field on the intensity of delayed fluorescence observed in the photolysis of anthracene in solution in chloroform (*a*) and dimethoxyethane (*b*) [80].

Numerous experimental studies have been devoted to the quenching of triplet states by free radicals (Table 5). In the presence of radicals, the DF lifetime is appreciably shortened and the effect of the magnetic field on the fluorescence intensity is of the opposite sign (the intensity increases with increase of the field strength). The usual mechanism for the process is

$$T + T \xrightarrow{k_a} S + S_0, \quad (40)$$

$$T + R \xrightarrow{k_R} S_0 + R, \quad (41)$$

$$T \xrightarrow{k_0} S, \quad (42)$$

where R is a quenching agent in a doublet state (free radical).

Table 5. Experimental results for the influence of the magnetic field on the quenching of triplet states by radical-ions.

| Reaction $R + T \rightarrow R + S_0$ | Concentration of radicals (molecules), M | Change in luminescence intensity, % (H = 8 kG)* | Method of recording | Refs. |
|---|---|---|---|---|
| Radical-cation of Würster's Blue + (Anthracene)$^T$ in $CH_2Cl_2$ | $1.8 \times 10^{-7}$ ($8.0 \times 10^{-5}$) | 2 | DF | 79 |
| | $2.1 \times 10^{-7}$ ($1.1 \times 10^{-3}$) | 6 | DF | 85 |
| | $3.6 \times 10^{-7}$ ($1.0 \times 10^{-7}$) | 9 | DF | 85 |
| *p*-Benzoquinone radical-anion + (Anthracene)$^T$ in $CH_2Cl_2$ | $1.6 \times 10^{-7}$ ($1.0 \times 10^{-3}$) | 3 | DF | 85 |
| Radical-cation of Würster's Blue + (Pyrene)$^T$ in dimethylformamide | $1.0 \times 10^{-3}$*** ($5.0 \times 10^{-3}$) | 8 | ECLF | 84 |
| | $1.0 \times 10^{-3}$ ($1.0 \times 10^{-3}$) | 20 | ECL | 84 |
| Radical-cation of Würster's Blue +(Rubrene)$^T$ in dimethylformamide | $1.5 \times 10^{-3}$ ($1.0 \times 10^{-3}$) | 30 | ECL | 86 |
| *p*-Benzoquinone radical-anion + (Rubrene)$^T$ in dimethylformamide | $2.4 \times 10^{-3}$ ($1.0 \times 10^{-3}$) | 15 | ECL | 86 |
| Rubrene radical-ion + + (Rubrene)$^T$ in dimethylformamide | $1.0 \times 10^{-3}$ | 12 | ECL | 86 |
| Radical-cation of Würster's Blue + (1,3,6,8-Tetraphenylpyrene)$^T$ in dimethylformamide | $0.23 \times 10^{-3}$ ($0.15 \times 10^{-3}$) | 26** | ECL | 86 |
| 10-Methylphenothiazine radical-cation + (Fluoranthene)$^T$ in dimethylformamide | $2.4 \times 10^{-3}$ ($3.0 \times 10^{-3}$) | 14 | ECL | 86 |
| Radical-cation of Würster's Blue +(Anthracene)$^T$ in dimethylformamide | $14.4 \times 10^{-3}$ ($10.3 \times 10^{-3}$) | 18 | ECL | 87 |
| Radical-cation of Würster's Blue + (9,10-Diphenylanthracene)$^T$ in dimethylformamide | $14.6 \times 10^{-3}$ ($10.5 \times 10^{-3}$) | 5 | ECL | 87 |
| Tri-*p*-tolylamine radical-cation + (9,10-Diphenylanthracene)$^T$ in tetrahydrofuran | $1.0 \times 10^{-3}$ ($1.0 \times 10^{-3}$) | 15 | ECL | 88 |

*The DF and ECL intensity increases in the magnetic field, indicating a decrease of the rate of reaction.
**H = 6 kG.
***For the ECL experiments, the "radical concentration" column lists the concentrations of the initial compounds from which the radical-ions are formed.

The magnetic field affects reactions (40) and (41) in the same way, decreasing the constants $k_a$ and $k_R$. However, it is readily seen that, when reaction (41) predominates over reaction (40), the DF intensity, determined by the overall concentration of triplets, will decrease in the magnetic field. The change in the nature of the influence of the magnetic field on DF can be readily traced when the relative concentration of radicals is varied (see Table 5): the effect increases with increasing concentration of the radical-ions.

Together with the DF method, electrogenerated chemiluminescence (ECL) has been widely used to investigate the effect of the magnetic field on elementary processes involving triplet states. The idea of such experiments is as follows. In an electrochemical cell containing an electrolyte (as a rule tetrabutylammonium perchlorate) and the test compound (for example, anthracene), the radical-ions $R^+$ and $R^-$ are produced. The subsequent processes are listed below:

$$R^+ + R^- \rightarrow R + T \quad \text{(electron transfer)},$$
$$R^+ + T \rightarrow R^+ + S_0 \quad \text{(quenching of triplets by radical-ions)},$$
$$T + T \rightarrow S + S_0 \quad \text{(triplet-triplet annihilation)},$$
$$R^+ + S \rightarrow R^+ + S_0 \quad \text{(quenching of singlet by radical-ions)},$$
$$T \rightarrow S \quad \text{(non-radiative processes), etc.}$$

The luminescence intensity due to the excited singlet states is recorded in the experiments.

Virtually all the systems in which the influence of the magnetic field on ECL was observed belong to the class of reactions with an "energy deficit", since the energy evolved on electron transfer is insufficient for the direct formation of the excited singlet state. It has been shown in a number of studies that in such systems the luminescence intensity increases with increasing magnetic field strength (up to 30%). This effect is usually explained by the fact that radical-ions play an important role in the reactions as triplet quenching agents. Since the excited states generated in ECL processes are formed together with radical-ions, the rate of quenching by the latter species undoubtedly constitutes the main factor influencing the luminescence intensity. The excited singlet states are quenched less effectively owing to their short lifetime. Table 5 presents the effects of the magnetic field for a single field strength $H \simeq 8$ kG in the systems investigated. Fig. 12 illustrates as an example the typical variation of the ECL intensity with the magnetic field. We may note that this type of variation is in full agreement with the theory of Atkins and Evans [33].

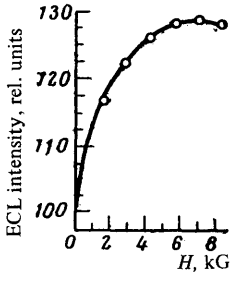



**Figure 12.** The influence of the magnetic field on the intensity of the electrogenerated chemiluminescence in a system containing rubrene and the radical-cation of Würster's Blue. [86]

The influence of the magnetic field on the quenching of the delayed fluorescence of anthracene and pyrene by molecular oxygen has been observed [81] (see Table 6). As for quenching by radicals, the magnetic field increased the DF intensity. The observed effect has been explained [81] by the following mechanism:

$$T + T \rightarrow S + S_0, \quad (43)$$

$$T + {}^3O_2 \rightarrow S + {}^1O_2. \quad (44)$$

**Table 6.** Experimental results for the influence of the magnetic field on the quenching of triplet states by oxygen [81].

| Reaction | Oxygen pressure, atm | Change in DF intensity, % ($H$ = 8 kG) |
|---|---|---|
| (Anthracene)$^T$ + (Anthracene)$^T$ in dimethylformamide* | 0 | −3 |
| | $3.0 \times 10^{-3}$ | +3 |
| | $6.0 \times 10^{-3}$ | +5 |
| (Pyrene)$^T$ + (Pyrene)$^T$ in dimethylformamide** | 0 | −2 |
| | $6.0 \times 10^{-3}$ | +1 |

*Anthracene concentration $2.1 \times 10^{-4}$ M.
**Pyrene concentration $2.6 \times 10^{-4}$ M.

At high oxygen concentrations, reaction (44) predominates and the DF intensity should therefore increase. The formation of singlet oxygen as a result of the reaction with an excited triplet hydrocarbon molecule [a reaction of type (44)] is probably the primary stage of the photochemical oxidation reaction. Since this reaction depends on the magnetic field, presumably the rate of photochemical oxidation of aromatic hydrocarbons is also sensitive to the magnitude of the magnetic field. The effect of the magnetic field in the photochemical oxidation reaction has so far been observed only in the solid phase [82]. The influence of the magnetic field on the surface conductivity of solid tetracene has been noted in the presence of oxygen [82]. The observed effect has been explained by the influence of the field on the photochemical oxidation reaction, leading to an increase of photoconductivity.

## XI. OTHER SYSTEMS

The two classes of processes examined do not exhaust all the systems in which effects of the magnetic field have been observed. The mechanisms of these effects in such instances can be regarded as fairly well understood, but, together with these, there have been reports of magnetic effects whose mechanism remains obscure.

There have been fairly numerous studies on the influence of the magnetic field on biochemical processes, including the effects of preliminary magnetisation. Polish workers [91-93] have published several reports about the influence of the magnetic field on reactions involving hydrogen peroxide. The effect of the preliminary magnetisation has also been observed in a number of instances. On the other hand, we may note that magnetic effects in the decomposition of hydrogen peroxide itself have not been observed [18]. Interesting data have been obtained by Hammond [94] in a study of the photochemical *cis–trans* isomerisation of stilbene and piperylene. The magnetic field (up to 9 kG) affects both the rate of reaction and the

steady-state photochemically generated isomer ratio when the reaction is sensitised by aromatic ketones. The magnitude of the effect is approximately 10%. On the other hand, the magnetic field has no influence when the process is carried out without a sensitiser.

The only available explanation of this effect, described in the literature, is similar to that of the explanation of the $\Delta g$ effect in radical pairs [95].

## XII. CONCLUSION

The influence of a constant magnetic field on processes involving free radicals and excited triplet states in solutions (radical recombination, triplet–triplet annihilation, quenching of triplet states by free radicals, the interaction of triplets with molecular oxygen, etc.), has now been reliably established and physically justified models of these phenomena have been proposed. The theoretical models are based on the postulate that the magnetic field alters the probability of the intercombination transition in pairs of reacting species. It is remarkable that even energetically weak influences (smaller than $kT$), such as hyperfine interactions and the difference between the Zeeman frequencies, can lead to appreciable effects of the magnetic field. The role of these interactions does not consist in overcoming energy barriers, but depends on the fact that they constitute a kind of "key", which may alter the multiplicity of the pair of reactants and result in their conversion from a multiplet, where the reaction is spin-forbidden, into a reactive state and conversely. Thus the effects of the magnetic field under consideration involve the manifestation of the spin prohibition rules in reactions of free radicals and triplet molecules. The magnetic isotope effect may be regarded as yet another important manifestation of spin prohibitions in radical recombination reactions. It is due to the fact that different nuclear isotopes differ in the magnitude of the hyperfine interaction responsible for the singlet–triplet transitions in the radical pairs.

Summarising the development of this research, one should note that the existing theoretical models describe satisfactorily the available experimental literature data not only qualitatively but also quantitatively. The range of processes in which magnetic effects may be observed, the scale of these effects, and the conditions most favourable for their observation have been clearly outlined.

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