

THE INFLUENCE OF PARAMAGNETIC IMPURITIES ON MAGNETIC EFFECTS IN RADICAL REACTIONS

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The influence of paramagnetic impurities on magnetic and spin effects in radical reactions in liquid solutions is treated. The recombination probability of a radical pair is obtained. It is shown, that at high impurity concentration or in high-viscosity solvents the effect of the magnetic field vanishes

1. Introduction

Magnetic and spin effects on radical reactions are well known [1]. They are connected with the existence of spin states of a radical pair (RP) and transitions between them. There are four RP electronic spin states: $|S\rangle$, $|T_-\rangle$, $|T_0\rangle$, $|T_+\rangle$. The stable product of most of the radical reactions is a singlet. Therefore, here and below we shall suppose, that the RP reacts only from the $|S\rangle$ state. The singlet-triplet (ST) transitions occur due to hyper-fine interaction, external magnetic field and electron-spin relaxation. These interactions result in a multiplicity change during the in-cage RP lifetime τ (i.e. the time of relative diffusion of radicals inside the reaction zone). So, the recombination probability p of the RP depends on the effectivity of ST transitions. A measure of the ST transitions effectivity is $\omega_{ST}\tau$, where ω_{ST} is the multiplicity change frequency.

Let us first consider the following two limit cases. If ST transitions are absent ($\omega_{ST}\tau \ll 1$), then only a quarter of the randomly met RPs are singlets. Therefore, the value of p for such RPs (diffusion RPs) differs from the result of the classical recombination theory [2] by the factor $\frac{1}{4}$ giving:

$$p_0 = \frac{1}{4}K\tau(1 + K\tau)^{-1}. \quad (1)$$

Here K (s^{-1}) is the recombination rate constant of a singlet RP in the reaction zone.

In the case of fast ST mixing ($\omega_{ST}\tau \gg 1$) the spin correlation of a RP decays rapidly. So, the RP recombination is independent of the initial spin state of the RP and the constant K is averaged over four spin states ($K \rightarrow \frac{1}{4}K$). Hence, one obtains

$$p_\infty = \frac{1}{4}K\tau(1 + \frac{1}{4}K\tau)^{-1}. \quad (2)$$

It is evident, that in the limit of a diffusion-controlled reaction ($K\tau \gg 1$) the value of p increases four times due to fast ST transitions.

The value of p is defined by the specific mechanisms of ST transitions in the intermediate case ($\omega_{ST}\tau \approx 1$). The most significant mechanisms are relaxation [3], Δg and hyper-fine interaction mechanisms [4,5] (see also ref. [1]).

In the present paper we consider the combined effect of the external magnetic field (Δg mechanism existing due to the difference of the Larmor precession frequencies of unpaired electrons) and the electron-spin relaxation (relaxation mechanism) on the recombination probability of the RP.

2. Recombination probability

The value of p will be calculated here in terms of the continual diffusion model [1,6,7]. The RP spin-density matrix satisfies between the contacts of radicals the stochastic Liouville equation:

$$\partial \rho(r, t) / \partial t = (i/\hbar) [\rho, \hat{H}] + \hat{R} \rho + D \nabla^2 \rho. \quad (3)$$

Here $D = D_1 + D_2$ is the diffusion coefficient for the relative motion of the radicals, r is the relative distance. The relaxation operator \hat{R} represents the RP spin relaxation and, for example, the Redfield description [8] may be used, \hat{H} is the RP spin hamiltonian. We shall consider the hyper-fine interaction to be small compared with the electron-spin relaxation. The corresponding criteria will be formulated below. Besides, the exchange interaction does not depend on the radical motion and recombination in a wide region of the RP parameters [6]. Therefore, we shall neglect exchange interaction. In this approximation the RP spin hamiltonian in the presence of an external magnetic field H_0 may be written in the form

$$\hat{H} = g_1 \beta H_0 \hat{S}_{1z} + g_2 \beta H_0 \hat{S}_{2z}. \quad (4)$$

where β is the Bohr magneton, \hat{S} is the electron-spin operator and g_1, g_2 are the g values of the radicals.

The usual boundary conditions for the RP spin-density matrix are

$$\left[D \partial \rho_{mn} / \partial r - \frac{1}{2} a K (\rho_{mn} \delta_{mS} + \rho_{mn} \delta_{nS}) \right]_{r=b} = 0, \quad (5)$$

where m, n denotes one of the S, T_-, T_0, T_+ states, a is the width of the reaction zone, b is the sum of the van der Waals radii of the radicals. The necessary boundary conditions at infinity are:

$$\rho_{mn}(\infty, t) = 0. \quad (6)$$

The initial conditions depend on the initial spin state of the RP. For example, in the case of an S precursor one has:

$$\rho_{mn}(r, 0) = [\delta(r - r_0) / 4\pi r^2] \delta_{mS} \delta_{nS}. \quad (7)$$

It means that at $t = 0$ all of the RPs of the ensemble are singlets and the relative distance is equal to r_0 . The initial conditions for the T_- , T_0 and T_+ -precursors are analogous. The conditions (5)–(7) completely define the solution of the system (3). It allows one to calculate the recombination probability of the RP as [1]

$$p = 4\pi b^2 a K \int_0^\infty \rho_{SS}(b, t) dt, \quad (8)$$

which takes into account all the re-encounters.

The representation of the relaxation operator \hat{R} in terms of the spin-spin and spin-lattice relaxation times $T_2^{(i)}$, $T_1^{(i)}$ is well known ($i = 1, 2$, the number of the radicals). So, the system (3) may be written in the

form:

$$\frac{\partial}{\partial t} \begin{pmatrix} \rho_{SS} \\ \rho_{T_0 T_0} \\ \text{Re } \rho_{ST_0} \\ \text{Im } \rho_{ST_0} \\ \rho_{T_- T_-} \\ \rho_{T_+ T_+} \end{pmatrix} = \begin{pmatrix} -(\tilde{\alpha} + \tilde{\beta}) & \tilde{\beta} - \tilde{\alpha} & 0 & -2\Omega & \tilde{\alpha} & \tilde{\alpha} \\ \tilde{\beta} - \tilde{\alpha} & -(\tilde{\alpha} + \tilde{\beta}) & 0 & 2\Omega & \tilde{\alpha} & \tilde{\alpha} \\ 0 & 0 & -2\tilde{\alpha} & 0 & \tilde{\gamma} & -\tilde{\gamma} \\ \Omega & -\Omega & 0 & -2\tilde{\beta} & 0 & 0 \\ \tilde{\alpha} & \tilde{\alpha} & 2\tilde{\gamma} & 0 & -2\tilde{\alpha} & 0 \\ \tilde{\alpha} & \tilde{\alpha} & -2\tilde{\gamma} & 0 & 0 & -2\tilde{\alpha} \end{pmatrix} \begin{pmatrix} \rho_{SS} \\ \rho_{T_0 T_0} \\ \text{Re } \rho_{ST_0} \\ \text{Im } \rho_{ST_0} \\ \rho_{T_- T_-} \\ \rho_{T_+ T_+} \end{pmatrix} + D \nabla^2 \begin{pmatrix} \rho_{SS} \\ \rho_{T_0 T_0} \\ \text{Re } \rho_{ST_0} \\ \text{Im } \rho_{ST_0} \\ \rho_{T_- T_-} \\ \rho_{T_+ T_+} \end{pmatrix}. \quad (9)$$

Here $\tilde{\alpha} = \frac{1}{4}(1/T_1^{(1)} + 1/T_1^{(2)})$, $\tilde{\beta} = \frac{1}{2}(1/T_2^{(2)} + 1/T_2^{(2)})$, $\tilde{\gamma} = \frac{1}{4}(1/T_1^{(2)} - 1/T_1^{(1)})$, $\Omega = (g_2 - g_1)\beta H_0/2\hbar$. By integrating (9) over time one obtains:

$$D \nabla^2 \begin{pmatrix} \Pi_{SS} \\ \Pi_{T_0 T_0} \\ A \\ B \\ \Pi_{T_- T_-} \\ \Pi_{T_+ T_+} \end{pmatrix} + \begin{pmatrix} -(\tilde{\alpha} + \tilde{\beta}) & \tilde{\beta} - \tilde{\alpha} & 0 & -2\Omega & \tilde{\alpha} & \tilde{\alpha} \\ \tilde{\beta} - \tilde{\alpha} & -(\tilde{\alpha} + \tilde{\beta}) & 0 & 2\Omega & \tilde{\alpha} & \tilde{\alpha} \\ 0 & 0 & -2\tilde{\alpha} & 0 & \tilde{\gamma} & -\tilde{\gamma} \\ \Omega & -\Omega & 0 & -2\tilde{\beta} & 0 & 0 \\ \tilde{\alpha} & \tilde{\alpha} & 2\tilde{\gamma} & 0 & -2\tilde{\alpha} & 0 \\ \tilde{\alpha} & \tilde{\alpha} & -2\tilde{\gamma} & 0 & 0 & -2\tilde{\alpha} \end{pmatrix} \begin{pmatrix} \Pi_{SS} \\ \Pi_{T_0 T_0} \\ A \\ B \\ \Pi_{T_- T_-} \\ \Pi_{T_+ T_+} \end{pmatrix} = - \begin{pmatrix} \rho_{SS}(r, 0) \\ \rho_{T_0 T_0}(r, 0) \\ 0 \\ 0 \\ \rho_{T_- T_-}(r, 0) \\ \rho_{T_+ T_+}(r, 0) \end{pmatrix}, \quad (10)$$

where $\Pi_{mn}(r) = \int_0^\infty \rho_{mn}(r, t) dt$, $A = \text{Re } \Pi_{ST_0}$, $B = \text{Im } \Pi_{ST_0}$. By summing and subtracting the first two and the last two equations respectively one may obtain the following three independent systems

$$D \nabla^2 A - 2\tilde{\alpha}A + \tilde{\gamma}\mu = 0, \quad D \nabla^2 \mu + 4\tilde{\gamma}A - 2\tilde{\alpha}\mu = \rho_{T_+ T_+}(r, 0) - \rho_{T_- T_-}(r, 0); \quad (11)$$

$$D \nabla^2 \Sigma - 2\tilde{\alpha}\Sigma + 2\tilde{\alpha}\eta = -(\rho_{SS}(r, 0) + \rho_{T_0 T_0}(r, 0)),$$

$$D \nabla^2 \eta + 2\tilde{\alpha}\Sigma - 2\tilde{\alpha}\eta = -(\rho_{T_- T_-}(r, 0) + \rho_{T_+ T_+}(r, 0)); \quad (12)$$

$$D \nabla^2 \Delta - 2\tilde{\beta}\Delta - 4\Omega B = -\rho_{SS}(r, 0) + \rho_{T_0 T_0}(r, 0), \quad D \nabla^2 B + \Omega\Delta - 2\tilde{\beta}B = 0. \quad (13)$$

Here $\eta, \mu = \Pi_{T_- T_-} \pm \Pi_{T_+ T_+}$, $\Sigma, \Delta = \Pi_{SS} \pm \Pi_{T_0 T_0}$. We shall restrict our attention to the latter two systems.

The boundary conditions for η , μ , Σ , Δ may be easily received from eqs. (5) and (6). The function $\Pi_{ss}(b)$ allows one to calculate the value of p in accordance with eq. (8).

Let us now write down the formulae obtained for p in case of various initial conditions. We shall suppose for simplicity that $r_0 = b$ and denote

$$\tau = \frac{ab}{D}, \quad x = \left(\frac{1}{2T_1^{(1)}} + \frac{1}{2T_1^{(2)}} \right) \frac{b^2}{D}, \quad y = \left(\frac{1}{T_2^{(1)}} + \frac{1}{T_2^{(2)}} \right) \frac{b^2}{D}, \quad z = \frac{\Omega b^2}{D},$$

$$f_{\pm}(y, z) = \left[\pm \frac{1}{2}y + \left(\frac{1}{4}y^2 + z^2 \right)^{1/2} \right]^{1/2}, \quad P(x) = 2 \left[1 + (2x)^{1/2} \right] / \left[2 + (2x)^{1/2} \right],$$

$$Q(y, z) = 1 + f_+(y, z) + f_-^2(y, z) / (1 + f_+(y, z) + K'\tau).$$

Here K' is the constant corresponding to the boundary condition (5) for the off-diagonal matrix element ρ_{ST_0} . In accordance with eq. (5) one obtains $K' = \frac{1}{2}K$, however the situation $K' > \frac{1}{2}K$ may occur [9]. So, we have

$$S \text{ precursor: } S_p = K\tau [K\tau + 2PQ/(P+Q)]^{-1}, \quad (14)$$

$$T_0 \text{ precursor: } T_0 p = K\tau [(Q-P)/(Q+P)] [K\tau + 2PQ/(P+Q)]^{-1}, \quad (15)$$

$$T_{\pm} \text{ precursor: } T_{\pm} p = K\tau [Q(P-1)/(Q+P)] [K\tau + 2PQ/(P+Q)]^{-1}. \quad (16)$$

The value of p of diffusion RPs is equal to

$$p = \frac{1}{4}S_p + \frac{1}{4}T_0 p + \frac{1}{4}T_+ p + \frac{1}{4}T_- p. \quad (17)$$

Using (14)–(16) one obtains:

$$p = \frac{1}{4}K\tau [2PQ/(P+Q)] [K\tau + 2PQ/(P+Q)]^{-1}. \quad (18)$$

The last expression is in agreement with eqs. (1) and (2) in case ST transitions are absent ($x, y, z = 0$) and in the case of fast relaxation mixing ($x, y \rightarrow \infty$). If the external magnetic field is high ($z \rightarrow \infty$), then

$$p'_{\infty} = \frac{1}{4}K\tau (1 + \frac{1}{2}K\tau)^{-1}. \quad (2')$$

The difference between (2) and (2') is due to the fact, that the electron-spin relaxation mixes all the four spin states, whereas the magnetic field induces only ST_0 transitions.

3. Discussion

The relaxation rate of the radicals is defined by their interaction with paramagnetic impurities such as O_2 , NO and Mn ions, present in the solvent or being the products of the reaction. There are the exchange and dipole–dipole interactions of the radical and impurity spins. In the last case we have [8]

$$\frac{1}{T_1} = \frac{16\pi^2}{5} \frac{g^2\beta^2\langle\mu^2\rangle C\eta RR'}{\hbar^2 kT^0 (R+R')^2} \left[\frac{1}{2}I(\omega - \omega') + \frac{3}{2}I(\omega) + 3I(\omega + \omega') \right], \quad (19)$$

$$\frac{1}{T_2} = \frac{16\pi^2}{5} \frac{g^2\beta^2\langle\mu^2\rangle C\eta RR'}{\hbar^2 kT^0 (R+R')^2} \left[I(0) + \frac{1}{4}I(\omega - \omega') + \frac{3}{4}I(\omega) + \frac{3}{2}I(\omega') + \frac{3}{2}I(\omega + \omega') \right]. \quad (20)$$

Here R , R' and ω , ω' are the radii and Larmor precession frequencies of the radical and impurity respectively, $\langle\mu^2\rangle$ is the mean square of the magnetic moment, C is the concentration of the impurity, T^0 is the temperature and η is the viscosity of the solvent, $\tau_c = (3\pi\eta/kT^0)RR'(R+R')$ is the correlation time of

impurity translation diffusion,

$$I(\omega) = \int_0^\infty J_{3/2}^2(u) \frac{u du}{u^4 + (\omega\tau_c)^2}.$$

Substituting the expressions (19) and (20) in eq. (18) we obtain the dependence of the recombination probability on the impurity concentration and the external magnetic field.

The expressions obtained may be easily generalized. If there is a difference between R and the size r of the localization region of the unpaired electron, then the radical mobility is defined by R and the minimal distance between unpaired electron and impurity is $r + R'$. It leads to the substitution $RR'/(R + R')^2 \rightarrow RR'/(r + R')(R + R')$ in eqs. (19) and (20).

In case when the external magnetic field is absent ($H_0 = 0$) the spin-spin and spin-lattice relaxation times are equal ($x = y$) and the value of p in the limit of a diffusion-controlled reaction ($K\tau \gg 1$) is equal to

$$p = 4[\sqrt{2}x + (\sqrt{2} + 1)\sqrt{x} + 1][\sqrt{2}x + (3\sqrt{2} + 2)\sqrt{x} + 4]^{-1} p_0. \quad (21)$$

The dependence of p on x is shown in fig. 1. In order to estimate the variation in p , let us assume $\mu \approx 2\beta$. Hence, in accordance with eqs. (19) and (20) one has

$$x = 3.2 \times 10^5 C \eta^2 R' R^2 r^2 / (r + R')(R + R'), \quad (22)$$

where R , C , η are expressed in cm, cm^{-3} and P respectively. We obtain for $R = 5 \text{ \AA}$, $r = 2 \text{ \AA}$, $R' = 1 \text{ \AA}$ $x \approx 2 \times 10^{-18} C \eta^2$. For liquids with low viscosity $\eta \approx 10^{-2} \text{ P}$ and for an impurity concentration at normal conditions $C \approx 10^{18} \text{ cm}^{-3}$ the variation in p is not considerable ($\approx 3\%$). However, if the viscosity of the liquid is high or if the concentration of the impurity is large, than the value of p varies considerably ($x = 1$, $p = 1.65 p_0$).

Let us consider now the RP recombination in a high external magnetic field ($H_0 > 1 \text{ kG}$). The magnetic field dependence of p at various impurity concentrations is shown in fig. 2. At $C = 0$ the expression (18) coincides with the previously obtained formula for the Δg -mechanism [1,9]. It is seen (fig. 2), that with increasing impurity concentration the effect of the magnetic field vanishes. The obtained result may be understood from the following qualitative consideration. At low magnetic field the relaxation mechanism dominates and, in agreement with fig. 1, the value of p increases with increasing impurity concentration. In the region of high magnetic field the Δg -mechanism dominates, hence expression (18) differs slightly from the well-known result [9] ($C = 0$).

The disappearance of the magnetic field effect in the presence of paramagnetic impurities may be

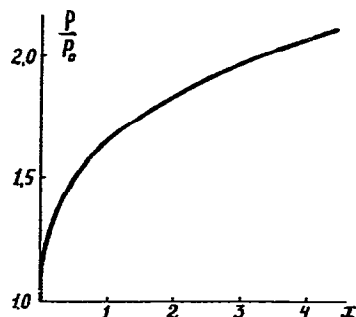


Fig. 1. The dependence of the recombination probability on x ($H_0 = 0$).

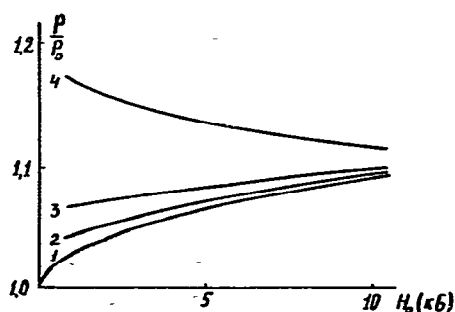


Fig. 2. The recombination probability as a function of external magnetic field at various impurity concentrations in the limit of diffusion-controlled reaction ($K\tau \gg 1$), $g_2 - g_1 = 10^{-3}$, $\eta = 10^{-2} \text{ P}$. Curve 1: $C = 0$, curve 2: $C = 10^{18} \text{ cm}^{-3}$, curve 3: $C = 10^{19} \text{ cm}^{-3}$, curve 4: $C = 10^{20} \text{ cm}^{-3}$.

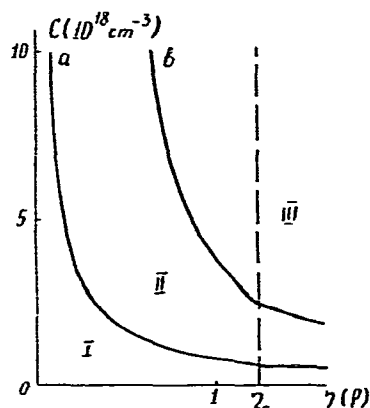


Fig. 3. The validity region of the obtained results.

realized, if the reaction product is a paramagnetic one. For example, the product of the decomposition of hydrogen peroxide by catalase is O_2 . In view of the large size and the complication of the catalase molecule the local concentration and the time of O_2 diffusion in the active zone of catalase may be large. It leads (see fig. 2) to the absence of the dependence of the recombination probability on external magnetic field. The independence of the rate of this reaction of the magnetic field was observed recently [10].

Let us now discuss the validity of the results obtained. The hyper-fine coupling constant of the organic radicals is of the order of 10 G. Hence, hyper-fine interaction may be disregarded in comparison with the electron-spin relaxation if

$$2.5 \times 10^{17}(r + R')(R + R')/RR' \ll C\eta. \quad (23)$$

The relaxation operator \hat{R} may be written in the form (9) if $T \gg \tau_c$ [8] or:

$$3 \times 10^{-5}(r + R')/R^2(R')^2 \gg C\eta^2. \quad (24)$$

Conditions (23) and (24) graphically represented by the curves a and b in fig. 3 divide the plane (C, η) into three regions. In region I hyper-fine interaction dominates and the dependence of p on the impurity concentration is negligible. In region II the obtained expressions are valid. In region III we cannot use the relaxation operator \hat{R} in the form (9). However, it is easy to estimate, that region III corresponds to the case where $x, y \gg I$, so the recombination probability approaches the asymptotic values (2), (2').

It is worth mentioning the possibility of fast electron-spin relaxation of the impurity. If the impurity relaxation time T' is less than τ_c , then τ_c must be substituted by T' in the expressions obtained above. Effectively, it leads to multiplying the right-hand sides of eqs. (19), (20), (23) and (24) by the factor η_c/η at $\eta > \eta_c$ (i.e. at $\tau_c > T'$, $\eta_c = T'[3\pi RR'(r + R')^2/kT^0(R + R')]^{-1}$ see fig. 3).

References

- [1] A.L. Buchachenko, R.Z. Sagdeev and K.M. Salikhov, Magnetic and spin effects in chemical reactions (Nauka, Novosibirsk, 1978).
- [2] L. Monchick, J. Chem. Phys. 24 (1956) 381.
- [3] B. Brocklehurst, Nature 221 (1969) 921.
- [4] R. Kaptein and J.L. Oosterhoff, Chem. Phys. Letters 4 (1969) 195, 214.
- [5] R.G. Lawler and G.T. Evans, Ind. Chim. Belge 36 (1971) 1087.
- [6] J.H. Freed and J.B. Pedersen, Advan. Magn. Reson. 8 (1976) 1.
- [7] Z. Shulten and K. Shulten, J. Chem. Phys. 66 (1977) 4616.
- [8] A. Abragam, The principles of nuclear magnetism (Clarendon Press, Oxford, 1961).
- [9] K.M. Salikhov, F.S. Sarvarov, Yu. N. Molin and R.Z. Sagdeev, Kinetika i Kataliz 16 (1975) 279.
- [10] V.K. Vanag, A.N. Kuznetsov and L.A. Piruzyan, Biofizika 28 (1983) 18.