

Application of integral encounter theory to account for the spin effects in radical reactions

I. Δg and spin relaxation effects on recombination kinetics of free radicals

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Abstract

Integral encounter theory is applied to investigate spin effects in radical recombination. Effects of electron spin relaxation and of S/T_0 mixing by an external magnetic field are considered. An analytical expression for the stationary rate constant is obtained from which appropriate conditions for experimental investigations are predicted. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Radical pairs (RP) are known to play an important role as reaction intermediates in many photochemical and radiation-induced processes [1,2]. Due to the spin conservation law in elementary chemical reactions only the singlet spin state of a RP is allowed to react to singlet recombination products. So the recombination probability depends upon the spin multiplicity of a RP. If a mechanism exists for changing the spin multiplicity it also affects the kinetics of radical recombination. Electron spin relaxation, hyperfine coupling of unpaired electrons with magnetic nuclei and spin dephasing in an external magnetic field are possible mechanisms of singlet–triplet (S–T) interconversion.

The statistics of radical encounters in solution differs much from that in the gas phase. The distinctive feature of reactions in liquid solution as opposed to the gas phase is the diffusional motion of the reacting particles with the essential role of re-encounters in the liquid solution. This leads to some difficulties in the theoretical description of reactions in solution. In solution, the general reaction scheme is as follows. An energized molecule dissociates or reacts to produce a spin-correlated pair of radicals which may react in the

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solvent “cage” or escape. Those radicals that avoid geminate recombination diffuse freely through the solution, where they may encounter radicals that have escaped from other geminate pairs to form non-correlated F-pairs (“freely diffusing pairs”). But even encounters of radicals in F-pairs give rise to spin correlation due to spin selective reaction. Mechanisms causing S–T interconversion may have a significant effect on reaction kinetics only if they can change the RP multiplicity within the lifetime of the RP in the cage, which for a pair of non-charged radicals can be estimated [1] as $\tau_d = R^2/D$, where R is the distance of closest approach and D is the interdiffusion coefficient. Typical values of τ_d range between 10^{-9} and 10^{-10} s [1].

Spin relaxation in normal organic radicals is usually too slow to meet this condition. However, in paramagnetic transition metal complexes typical relaxation times are in the range of 10^{-9} – 10^{-13} s [3]. For example, for paramagnetic complexes of Ru(III) and for the ferricenium cation the longitudinal electron spin relaxation time is on the order of 10 ps [4,5]. The short spin relaxation time in these species is due to their strong spin–orbit coupling which also causes considerable deviations of the g -factors of these species from the values of organic counter radicals. Thus, in an external magnetic field the Larmor dephasing of the two electron spins in such a radical pair generates effective T/S mixing. This affects the geminate kinetics leading e.g. to a magnetic-field dependence of the cage escape efficiency of these radicals when photochemically created in geminate pairs of a paramagnetic transition metal complex and an organic radical. For experimental and theoretical investigations of such effects see Refs. [4–12].

The effect of electron spin relaxation on bulk radical recombination was previously studied theoretically by Sarvarov [13] and Sarvarov and Salikhov [14] who used the exponential model of RP kinetics which is not generally adequate. A consistent approach for the description of bimolecular reactions in solution should take into account diffusional motion of the reactants, distance-dependent reaction probability, and the presence of different internal states in the reactants. This is a very complicated many-particle problem. Fortunately, in typical cases the concentration of reacting particles in solution can be considered as low, i.e. the volume fraction of reactants in the solution is small. Most modern theoretical approaches to many-particle reaction systems in solution imply and use this assumption.

Approximately 25 years ago the so-called impact approximation [3,15,16] was elaborated for the theoretical description of spin-selective processes such as spin exchange and radical recombination in solutions. This approximation was based on an intuitive generalization of the Smoluchovsky [17] approach and the internal states of reacting particles were taken into account. This impact approximation is actually a liquid-phase analogue of the so-called impact theory of pressure broadening of spectral lines and multiplets in a gas phase [18,19], where collision is considered as an instantaneous impact changing populations and phases of internal states of colliding particles (such approximation allows to describe well the central part of a spectrum). The kinetic equations obtained are of the type of normal chemical rate equations. A recipe was given how to calculate reaction rate constants through microscopic parameters of reactions (exchange integral, recombination probability, diffusion coefficient etc.). Shortly after, in a set of papers [20,21], a consistent derivation of the kinetic equations employing integro–differential convolution equations for the time-dependence of reactant concentrations was presented. This theory is now known as integral encounter theory (IET). It was shown that under some assumptions these exact equations can be reduced to the equations of impact approximation theory which have the form of chemical rate equations but that this is not generally possible. For example, reversible reactions with metastable reactants have a non-stationary character from the beginning to the end and cannot be described in the frame of chemical rate equations, but only in the formalism of IET [22]. Although the original IET was elaborated about 25 years ago, only recently it has been recognized as a unique and universal key to multistage transfer reactions between A and B particles in dilute solutions. This was demonstrated with a number of reaction scenarios including sequential bimolecular and geminate stages. Another important feature of IET is its matrix formulation. It allows to include as many intra-molecular states as necessary, using the vectors

$$N_A = \begin{pmatrix} N_1^A \\ N_2^A \\ \vdots \\ N_n^A \end{pmatrix} \quad \text{and} \quad N_B = \begin{pmatrix} N_1^B \\ N_2^B \\ \vdots \\ N_m^B \end{pmatrix},$$

whose components represent the state densities of reactants and reaction products. This is the way how IET accounts for monomolecular decay or interconversion accompanied by bimolecular transfer processes. It can also take into account a quasi-resonant internal structure in the reactants (i.e. with level splittings less than thermal energy kT). In this case the vectors N_A and N_B should be replaced by density matrices σ_A and σ_B .

IET has been applied to the description of the kinetics of electron and excitation transfer processes where the spin nature of reacting particles is not significant and is not taken into account [22–29]. This work is the first attempt to apply IET to processes where the spin nature of reacting particles plays an essential role. We derive kinetic equations and determine rate constants of radical recombination processes under conditions where paramagnetic relaxation has to be taken into account. When attempting a treatment of this problem in the frame of the impact approximation we found that the elements of the impact operator cannot be calculated unambiguously (see Appendix A). Although the impact approximation was successfully used for the calculation of rate constants for a number of reactions including bimolecular radical recombination in an external magnetic field (albeit in the absence of paramagnetic relaxation) our attempts to apply it for this more general situation failed. So, in this case, we had to start from the first principles of IET. As we have shown, the transition to the usual rate constant description is only possible in the final equations of IET and only in cases where the Boltzman population difference of radical spin levels can be neglected and where they are equally populated at the beginning.

In this paper, kinetic effects on the bulk recombination of radicals caused by electron spin relaxation and by Larmor dephasing in an external magnetic field are theoretically investigated. The kinetic equations that describe the time evolution of the one-particle density matrix were obtained using integral encounter theory. An analytical expression for the bimolecular rate constant of bulk recombination was derived and its dependence on electron relaxation time was analyzed.

2. Formal theory

If a contact reaction of non-paramagnetic species is considered, the expression for the reaction rate constant is well known [30]:

$$k = \frac{k_r k_d}{k_r + k_d}.$$

Here k_r is the rate constant of contact reaction (or kinetic rate constant). For contact reaction within a spherical layer of radius R , width Δ and reaction probability per unit of time W_0 , $k_r = 4\pi R^2 \Delta W_0$; k_d is the diffusional rate constant, $k_d = 4\pi R D$, D is the interdiffusion coefficient. It is clear that for spin selective reaction, interactions causing S–T interconversion will also affect reaction kinetics.

The effect of an external magnetic field on bulk radical recombination was first considered in Ref. [14]. For the calculation of the recombination rate constant the impact approximation was used. The impact approximation allows one to obtain a kinetic equation for the one-particle density matrix that describes the evolution of the internal states of the particle and accounts for re-encounters of reactants. However, the impact approximation fails to describe reactions of metastable particles [22]. As shown in Appendix A, the impact approximation also fails in the case of relaxing particles. This shortcoming of the impact approximation is overcome by IET. For the reaction between two particles, A and B, each with internal

structure IET yields the following kinetic equation for the ensemble-averaged one-particle density matrix σ_A [21,22]:

$$\frac{d\sigma_A(t)}{dt} = \hat{L}_A \sigma_A(t) + C_B^0 \text{Tr}_B \int_0^t \hat{M}(\tau) \sigma_A(t-\tau) \otimes \sigma_B(t-\tau) d\tau. \quad (1)$$

Here C_B^0 is the initial concentration of particles B, \hat{L}_A is the Liouville super operator for particle A describing the evolution of its internal states. This Liouvillian does not depend on inter-radical distance. The time-related Laplace transform of the memory operator $\hat{M}(t)$ is [22]

$$\hat{M}(s) = \int \hat{W}(\vec{r}) \hat{F}(\vec{r}, s) [s - \hat{L}] d\vec{r}, \quad (2)$$

where $\hat{W}(\vec{r})$ is the distance dependent reaction operator, $\hat{L} = \hat{L}_A + \hat{L}_B$ is the Liouville super operator of the RP. It corresponds to the direct sum of the internal Liouville operators of the separate radicals and does not depend on inter-radical distance. The operator $\hat{F}(\vec{r}, \tau)$ obeys the equation

$$\frac{\partial \hat{F}(\vec{r}, \tau)}{\partial \tau} = \hat{L} \hat{F}(\vec{r}, \tau) + \hat{W}(\vec{r}) \hat{F}(\vec{r}, \tau) + \hat{\mathcal{L}}(\vec{r}) \hat{F}(\vec{r}, \tau) \quad (3)$$

with the initial condition $\hat{F}(\vec{r}, 0) = \hat{E}$. Here $\hat{\mathcal{L}}(\vec{r})$ is the functional operator determined by the type of motion, \hat{E} is the identity operator. If diffusional motion of non-charged particles is considered $\hat{\mathcal{L}}(\vec{r}) = D\nabla^2 = D\Delta$, where D is the interdiffusion coefficient.

Eqs. (1)–(3) provide the basis of integral encounter theory appropriate for arbitrary lifetime of the particles and arbitrary interactions between them.

One can also represent Eq. (3) in equivalent integral form [22]:

$$\hat{F}(\vec{r}, s) = (s - \hat{L})^{-1} + \int \hat{\mathcal{G}}(\vec{r}, \vec{r}', s) \hat{W}(\vec{r}') \hat{F}(\vec{r}', s) d\vec{r}', \quad (4)$$

where

$$\hat{\mathcal{G}}(\vec{r}, \vec{r}', s) = \int_0^\infty \varphi(\vec{r}, \vec{r}', t) \exp(\hat{L}t) \exp(-st) dt \quad (5)$$

and $\varphi(\vec{r}, \vec{r}', t)$ is the Green's function of equation

$$\dot{\varphi}(\vec{r}, \vec{r}', t) = \hat{\mathcal{L}}(\vec{r}) \varphi(\vec{r}, \vec{r}', t), \quad \varphi(\vec{r}, \vec{r}', 0) = \delta(\vec{r} - \vec{r}'). \quad (6)$$

If the reaction is due to short-range interactions, the theory may be developed further using the so-called kinematic approximation [31]. It is based on the assumption that one may neglect reactions at any distance greater than the distance of closest approach R , so the width of reaction zone $\Delta \ll R$. Within the limits of the kinematic approximation the following expression for the memory operator is found [22]

$$\hat{M}(s) = \hat{k}_r [\hat{E} - \hat{g}(s) \hat{W}(R)]^{-1}. \quad (7)$$

$\hat{k}_r = \int \hat{W}(r) d\vec{r} \approx \hat{W}(R)v$, $v = 4\pi R^2 \Delta$ is the reaction volume. Operator $\hat{g}(s)$ is defined as

$$\hat{g}(s) = \int_0^\infty f(t) e^{(\hat{L}-s)t} dt \quad (8)$$

and $f(t)$ is a kinematic function characterizing the relative motion of the reactants:

$$f(t) = \int_v \varphi(R, \vec{r}', t) d\vec{r}' \approx \frac{1}{v} \int_v \int_v \varphi(r, r', t) d\vec{r} d\vec{r}'. \quad (9)$$

Expression (7) gives an algebraic recipe to find the kernel of kinetic Eq. (1) when $\hat{g}(s)$ is known. Matrix elements of $\hat{g}(s)$ may be expressed in terms of the Laplace transform $g(s)$ of the function $f(t)$:

$$g(s) = \int_0^{\infty} f(t) \exp(-st) dt. \quad (10)$$

Actually, by this method the problem of determining the reaction rate constant for a complicated reaction which includes the internal states of reactants is reduced to the much easier problem of finding the function $g(s)$ defined through the Laplace transform $\varphi(r, r', s)$ of the Green's function of free motion of the particles in the *absence of reaction* $\varphi(r, r', t)$. The value of $g(s)$ corresponds to the average value of $\varphi(r, r', s)$ over the reaction zone. There are a number of analytical expressions and approximations for $g(s)$ for different models of reactant motion such as the model of continuous diffusion [32], stochastic jump model [33,34], diffusion of reactants in their mutual coulomb potentials [35,36]. The function $g(s)$ has also been defined for systems with reaction anisotropy [32]. Although $\varphi(r, r', t)$ does not depend on reaction and, therefore, not on reaction anisotropy, its average value over the reaction zone, i.e. $g(s)$, depends on the shape of this zone. For a particular type of motion, $g(s)$ can be calculated at least by numerical solution of Eq. (6) and then be used in tabulated form to calculate the kinetics of contact reactions with this particular type of motion.

If diffusional motion of non-charged reacting particles is considered, $g(s)$ is given by the expression [32]

$$g(s) = \frac{\tau_e}{1 + \sqrt{s\tau_d}}, \quad (11)$$

where $\tau_e = R\Delta/D$ is the average residence time in the reaction zone and $\tau_d = R^2/D$ is the average encounter duration.

When bimolecular reactions in homogeneous solution are considered it is usually supposed that all spin states are equally populated and there is no coherence between them. In Ref. [37] where the impact approximation was applied to the description of radical recombination it was shown that the kinetic equations conserve the initial property of the one-particle density matrix of being proportional to the unit matrix. Thus the set of differential equations for the elements of the one-particle density matrix may be reduced to give a closed equation for the concentrations. In Appendix B restrictions on the Liouville operator are obtained ensuring that the kinetic equations of IET conserve the initial equality of populations and the absence of coherence between radical spin states.

3. Model

The further theoretical treatment will refer to the homogeneous radical recombination reaction as represented in Fig. 1. It implies that radicals ^2A and ^2B have uniform initial distribution as is the case e.g.

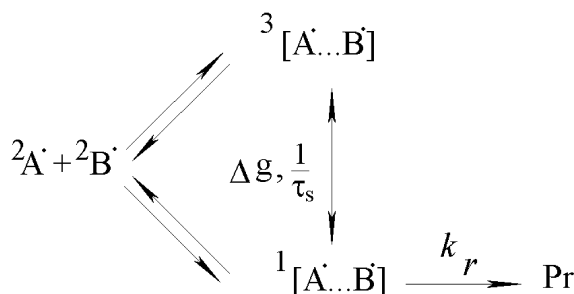


Fig. 1. Homogeneous stage of backward electron transfer reaction.

for the bulk recombination of photochemically or radiation-chemically generated radicals. Fig. 1 also implies that radicals can recombine only from the singlet state of the encounter complex $^1[A \cdots B]$ i.e. from the singlet state of a RP. Electron spin relaxation in one of the radicals (the paramagnetic complex) is assumed to represent a major channel of S–T conversion. Due to non-equal g -factors of the radicals an external magnetic field may also contribute to S–T transitions. The effect of g -tensor anisotropy will be the subject of further investigations and will not be taken up here. Relaxation in the second radical (an organic radical) will not be accounted for, and $T_1 = T_2 \equiv \tau_s$ will be assumed for the relaxation times of the paramagnetic transition metal complex. Furthermore, τ_s is assumed to be independent of an external magnetic field. These are realistic assumptions if spin relaxation is due to an Orbach mechanism [38] involving thermal population of low lying electronic states as applies for the Ru(III) and ferrocenium systems that have been of spin chemical interest [4,5]. These assumptions are also valid if spin–rotational coupling is the dominant relaxation mechanism [39].

4. Calculations

The following notations for the indices of the *one-particle* density matrix will be used: $\alpha\alpha = 1$, $\beta\beta = 2$, $\alpha\beta = 3$, $\beta\alpha = 4$, for example, $\sigma_{\alpha\beta}^A \equiv \sigma_3^A$. The direct product $\hat{\sigma} = \hat{\sigma}_A \otimes \hat{\sigma}_B$ indices will be further denoted as $\sigma_{ik} \equiv \sigma_i^A \sigma_k^B$. This matrix basis will be referred to as the factorized basis.

$$\hat{\sigma} = \begin{bmatrix} \sigma_{11} \\ \sigma_{12} \\ \vdots \\ \sigma_{43} \\ \sigma_{44} \end{bmatrix}. \quad (12)$$

These notations introduced for the density matrix allow for a considerable simplification of the two-particles operators.

Let us denote the relaxing particle as B. In this case the relaxation super operator will take the form

$$\hat{\hat{Q}} = \begin{bmatrix} \hat{Q}_B & 0 & 0 & 0 \\ 0 & \hat{Q}_B & 0 & 0 \\ 0 & 0 & \hat{Q}_B & 0 \\ 0 & 0 & 0 & \hat{Q}_B \end{bmatrix}, \quad \hat{Q}_B = \begin{bmatrix} -\frac{1}{2\tau_s} & \frac{1}{2\tau_s} & 0 & 0 \\ \frac{1}{2\tau_s} & -\frac{1}{2\tau_s} & 0 & 0 \\ 0 & 0 & -\frac{1}{\tau_s} & 0 \\ 0 & 0 & 0 & -\frac{1}{\tau_s} \end{bmatrix}, \quad (13)$$

where τ_s is the electron spin relaxation time of the particle B ($T_1 = T_2 = \tau_s$).

The operator representing the Zeeman interaction between electron spin and external magnetic field is

$$\hat{L}_{A,B}^0 = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & g_{A,B}\beta H & 0 \\ 0 & 0 & 0 & -g_{A,B}\beta H \end{bmatrix} \quad (14)$$

for particle A or B, respectively. In the factorized basis the two-particle operator of the Zeeman interaction is

$$\hat{L}^0 = \begin{bmatrix} \hat{L}_B^0 & 0 & 0 & 0 \\ 0 & \hat{L}_B^0 & 0 & 0 \\ 0 & 0 & \hat{L}_B^0 + g_A \beta H & 0 \\ 0 & 0 & 0 & \hat{L}_B^0 - g_A \beta H \end{bmatrix}. \quad (15)$$

The total Liouville operator, in view of relaxation, may be written as

$$\hat{L} = \hat{L}^0 - i\hat{Q} = \begin{bmatrix} \hat{L}_B & 0 & 0 & 0 \\ 0 & \hat{L}_B & 0 & 0 \\ 0 & 0 & \hat{L}_B + g_A \beta H & 0 \\ 0 & 0 & 0 & \hat{L}_B - g_A \beta H \end{bmatrix}, \quad (16)$$

$$\hat{L}_B = \hat{L}_B^0 - i\hat{Q}_B.$$

The operator $\hat{g}(s)$ corresponding to the Liouville operator (16) is given in explicit form in Appendix C.

4.1. Case of recombination only from the singlet radical pair state

Let us now consider the case when the reaction is allowed only from the singlet spin state of the RP. The non-zero elements of the recombination operator for this case are represented in Table 1 and in Appendix D.

One can see that the Liouville operator (16) obeys Eq. (B.1). Thus the set of integro-differential equation (1) may be reduced to give the closed equation on concentration:

$$\frac{dC(t)}{dt} = \frac{1}{4} \int_0^t m(t-\tau) C^2(\tau) d\tau \quad (17)$$

with the kernel $m(t)$ defined by Eq. (B.4) (see Appendix B), whose Laplace transform $\tilde{m}(s)$ is given by

$$\tilde{m}(s) = -k_r \frac{1 + \frac{W_0}{4}(x_4^2 + x_3^3)}{1 + \frac{W_0}{2}(x_4^2 + x_3^3 + x_1^1) + \frac{W_0^2}{8}(2x_4^2 x_3^3 + x_1^1(x_4^2 + x_3^3))}. \quad (18)$$

The coefficients x_i^j are defined in Appendix C. The symbol W_0 denotes the contact reaction probability per unit time from the singlet state of the RP. Using a well-known recipe [40–43] for the case when $m(t-\tau)$ changes in time much faster then the $C(t)$, one may re-write integral kinetic equation (17) as a differential one:

$$\frac{dC(t)}{dt} = -k(t)C^2(t), \quad (19)$$

Table 1
Non-zero elements of recombination operator for the case of recombination allowed only from the singlet spin state

$\hat{W}_{ik,lm}$	
$\hat{W}_{12,12}, \hat{W}_{21,21}, \hat{W}_{34,34}, \hat{W}_{43,43}$	$-W_0/2$
$\hat{W}_{13,13}, \hat{W}_{31,31}, \hat{W}_{14,14}, \hat{W}_{41,41}, \hat{W}_{23,23}, \hat{W}_{32,32}, \hat{W}_{24,24}, \hat{W}_{42,42}$	$-W_0/4$
$\hat{W}_{34,12}, \hat{W}_{43,12}, \hat{W}_{34,21}, \hat{W}_{43,21}, \hat{W}_{13,31}, \hat{W}_{31,13}, \hat{W}_{14,41}, \hat{W}_{41,14},$ $\hat{W}_{23,32}, \hat{W}_{32,23}, \hat{W}_{24,42}, \hat{W}_{42,24}, \hat{W}_{12,34}, \hat{W}_{12,43}, \hat{W}_{21,34}, \hat{W}_{21,43}$	$W_0/4$

where the time-dependent rate constant is

$$k(t) = -\frac{1}{4} \int_0^t m(\tau) d\tau.$$

It starts from $k(t=0) = k_r/4$ and reaches a stationary value k :

$$k = \lim_{t \rightarrow \infty} k(t)$$

at $t \rightarrow \infty$. With relations (C.3), (C.10), and (C.13) from Appendix C one can get

$$\lim_{s \rightarrow 0} x_1^1 = \frac{1}{2}(g(0) + g(1/\tau_s)), \quad (20)$$

$$\lim_{s \rightarrow 0} x_4^2 = g(1/\tau_s - i(g_A - g_B)\beta H), \quad (21)$$

$$\lim_{s \rightarrow 0} x_3^3 = g(1/\tau_s + i(g_A - g_B)\beta H). \quad (22)$$

Taking into account expressions (20)–(22) and the well-known relation [44]

$$\lim_{t \rightarrow \infty} k(t) = \lim_{s \rightarrow 0} s\tilde{k}(s),$$

we obtain the *stationary* rate constant

$$k = \lim_{t \rightarrow \infty} k(t) = -\frac{1}{4} \lim_{s \rightarrow 0} \tilde{m}(s) = \frac{k_r}{4} \frac{1 + \frac{w_0}{4} \Sigma_\omega}{1 + \frac{w_0}{4} (\Sigma_0 + 2\Sigma_\omega) + \frac{w_0^2}{16} (4\Pi + \Sigma_0 \Sigma_\omega)}. \quad (23)$$

The notations used are the following:

$$\Sigma_0 = g(0) + g\left(\frac{1}{\tau_s}\right),$$

$$\Sigma_\omega = g\left(\frac{1}{\tau_s} + i\omega\right) + g\left(\frac{1}{\tau_s} - i\omega\right),$$

$$\Pi = g\left(\frac{1}{\tau_s} + i\omega\right)g\left(\frac{1}{\tau_s} - i\omega\right),$$

$$\omega = |\Delta g|\beta H, \quad \Delta g = g_A - g_B.$$

It is worth noting that the stationary reaction rate constant (23) is expressed in terms of a $g(s)$ function and as was mentioned above it can be easily generalized to an arbitrary type of motion of the reactants and their reactivity anisotropy. In the special case of continuous diffusion $g(s)$ is given by Eq. (11).

It is interesting to compare the result (23) of our treatment in case of continuous diffusion with those of the following simplified approach relating this problem to the geminate RP problem. Consider the solutions of the cage-escape problem for geminate pairs, created in singlet, or triplet. Let the cage-escape yields for these be denoted $\varphi_{S,ce}$ and $\varphi_{T_0,ce}$, $\varphi_{T_+,ce}$, $\varphi_{T_-,ce}$, respectively. Then the rate constant k can be expressed as

$$k = \frac{k_d}{4} ((1 - \varphi_{S,ce}) + (1 - \varphi_{T_0,ce}) + (1 - \varphi_{T_+,ce}) + (1 - \varphi_{T_-,ce})). \quad (24)$$

In fact, substituting the special form of $g(s)$ for continuous diffusion given by Eq. (11) into Eq. (23) yields the same result as when substituting the analytical solutions for the cage escape yields given in Ref. [45] into Eq. (24).

4.2. Case of radical pair recombination with reactivity distributed over spin substates

Due to the strong spin–orbit coupling when reactions of paramagnetic transition metal complexes are considered one should usually operate not with pure spin states but with effective ones [6]. In this case the singlet character, p_i^S , of effective spin state ($i = S', T'_0, T'_{+}, T'_{-}$) is usually introduced. Then the contact recombination probability per unit time for state i is given by $p_i^S W_0$. The non-zero elements of the recombination operator for this case are given in Table 2 of Appendix D.

Having

$$p_S^S + p_{T_0}^S + p_{T_+}^S + p_{T_-}^S = 1 \quad (25)$$

and assuming $p_{T_+}^S = p_{T_-}^S$ we managed to obtain expressions for the Laplace transform of the time-dependent reaction rate constant. In general, the dependence of the stationary reaction rate constant on the parameters of the reacting system is given by a bulky expression. In the case of $p_{T_+}^S = p_{T_-}^S = 0$, that is of interest in the spin chemistry of ferrocenes [4], it can be simplified to give for zero field

$$k = \frac{k_r}{4} \frac{1 + 2p_S^S(1 - p_S^S)W_0g(1/\tau_s)}{1 + \frac{W_0}{4}(g(0) + 3g(1/\tau_s)) + \frac{W_0^2}{2}p_S^S(1 - p_S^S)g(1/\tau_s)(g(0) + g(1/\tau_s))} \quad (26)$$

and for the limiting case of $\omega \rightarrow \infty$

$$k = \frac{k_r}{4} \frac{1}{1 + \frac{W_0}{4}(g(0) + g(1/\tau_s))}. \quad (27)$$

For the case of $p_{T_0}^S = 0$, $p_{T_+}^S = p_{T_-}^S$, which is the typical situation for the spin chemistry of Ru(III) complexes [6], the zero field result is

$$k = \frac{k_r}{4} \frac{1 + \frac{3}{2}W_0p_S^S(1 - p_S^S)g(1/\tau_s)}{1 + \frac{W_0}{4}(g(0) + g(1/\tau_s)(1 + 2p_S^S)) + \frac{W_0^2}{8}p_S^S(1 - p_S^S)g(1/\tau_s)(3g(0) + g(1/\tau_s))}, \quad (28)$$

whereas in the limiting case of $\omega \rightarrow \infty$ one obtains

Table 2

Non-zero elements of recombination operator for recombination from RP spin states according to their singlet character

$\hat{W}_{ik,lm}$	
$\hat{W}_{11,11}$	$-W_0p_{T_+}^S$
$\hat{W}_{22,22}$	$-W_0p_{T_-}^S$
$\hat{W}_{12,12}, \hat{W}_{21,21}, \hat{W}_{34,34}, \hat{W}_{43,43}$	$-(W_0/2)(p_S^S + p_{T_0}^S)$
$\hat{W}_{33,33}, \hat{W}_{44,44}$	$-(W_0/2)(p_{T_+}^S + p_{T_-}^S)$
$\hat{W}_{13,13}, \hat{W}_{31,31}, \hat{W}_{14,14}, \hat{W}_{41,41}$	$-(W_0/4)(p_S^S + p_{T_0}^S + 2p_{T_+}^S)$
$\hat{W}_{23,23}, \hat{W}_{32,32}, \hat{W}_{24,24}, \hat{W}_{42,42}$	$-(W_0/4)(p_S^S + p_{T_0}^S + 2p_{T_-}^S)$
$\hat{W}_{34,12}, \hat{W}_{43,12}, \hat{W}_{34,21}, \hat{W}_{43,21}, \hat{W}_{13,31}, \hat{W}_{31,13},$ $\hat{W}_{14,41}, \hat{W}_{41,14}, \hat{W}_{23,32}, \hat{W}_{32,23}, \hat{W}_{24,42}, \hat{W}_{42,24},$ $\hat{W}_{12,34}, \hat{W}_{12,43}, \hat{W}_{21,34}, \hat{W}_{21,43}$	$(W_0/4)(p_{T_0}^S - p_S^S)$

$$k = \frac{k_r}{4} \frac{1 + p_S^S(1 - p_S^S)W_0g(1/\tau_s)}{1 + \frac{W_0}{4}(g(0) + g(1/\tau_s)) + \frac{W_0^2}{4}p_S^S(1 - p_S^S)g(0)g(1/\tau_s)}. \quad (29)$$

5. Discussion

5.1. Remote electron transfer

The results (23), (26)–(29) were obtained under the assumption that the reaction zone is thin enough to neglect any spin evolution of the RP during the average time spent in reaction zone $\tau_e = RA/D$. When this is not the case one has to account for the spin evolution of the RP during the time τ_e . Such a situation applies when the relaxation times of the reacting particles are comparable with the average time spent in the reaction zone $\tau_e = RA/D$. So in this case it might be essential to account for the relaxation effect during the time spent in the reaction zone. For the important case of continuous diffusion the following modified expression for $g(s)$ was obtained in Ref. [46].

$$g(s) = \frac{\tau_e}{1 + \sqrt{s\tau_d} + s\tau_e}. \quad (30)$$

When substituting this expression into Eq. (26) the following result for $p_S^S = 1$ is obtained in the absence of a magnetic field

$$k = \frac{1}{4} \frac{k_d k_r}{k_d + \frac{k_r}{4} \left(1 + \frac{3}{1 + \sqrt{\tau_d/\tau_s + \tau_e/\tau_s}} \right)}. \quad (31)$$

5.2. Limiting cases

Let us now consider the limiting cases of formula (23) accounting for diffusive motion of the reacting particles and singlet character of recombination ($p_S^S = 1$). For further analysis we will specialize to the case of continuous diffusion, i.e. we will use Eq. (11) for $g(s)$. Furthermore, we make use of the relations

$$W_0\tau_e = W_0RA/D = k_r/k_d$$

where, as was already indicated, $k_r = 4\pi R^2\Delta W_0$, $k_d = 4\pi RD$.

In the case of extremely fast relaxation $\tau_s \ll \tau_d$ one can easily obtain

$$k = \frac{k_d \frac{k_r}{4}}{k_d + \frac{k_r}{4}} = \frac{k_d}{1 + 4 \frac{k_d}{k_r}}. \quad (32)$$

This corresponds to fast transitions, maintaining equilibrium between all the four collective spin states throughout the reaction. It causes an effective reduction of the kinetic rate constant k_r by a factor of 4.

Having $\tau_s \gg \tau_d$ one can obtain from Eq. (23)

$$k = \frac{k_r k_d}{4} \frac{k_d(1 + \omega\tau_d + \sqrt{2\omega\tau_d}) + \frac{k_r}{4}(2 + \sqrt{2\omega\tau_d})}{k_d^2(1 + \omega\tau_d + \sqrt{2\omega\tau_d}) + \frac{k_r k_d}{2}(3 + \omega\tau_d + 2\sqrt{2\omega\tau_d}) + \frac{k_r^2}{8}(4 + \sqrt{2\omega\tau_d})}. \quad (33)$$

Exactly the same result was obtained by Sarvarov [13] and Sarvarov and Salikhov [14] using the impact approximation. In the case of high reactivity they obtained the following result [14]:

$$k = \frac{k_r k_d}{4} \frac{2 + \sqrt{2\omega\tau_d}}{\frac{k_r}{2}(4 + \sqrt{2\omega\tau_d}) + k_d(2 + \sqrt{2\omega\tau_d})}. \quad (34)$$

Although in the general case not identical analytically, expressions (33) and (34) give very similar results for a wide range of parameters. For zero magnetic field equations (33) and (34) yield the same result for k :

$$k = \frac{1}{4} \frac{k_d k_r}{k_d + k_r}. \quad (35)$$

Identity of Eqs. (33) and (34) is also found in the limiting case of high magnetic field ($\omega \rightarrow \infty$). Then the expressions for k reduce to

$$k = \frac{1}{4} \frac{k_d k_r}{k_d + \frac{k_r}{2}}. \quad (36)$$

For zero field, Eq. (23) is reduced (taking into account (11)) to

$$k = \frac{k_d \frac{k_r}{4}}{k_d + \frac{k_r}{4} \left(1 + \frac{3}{1 + \sqrt{\tau_d/\tau_s}} \right)}, \quad (37)$$

which for slow relaxation, $\tau_s \gg \tau_d$, gives the standard expression for the bimolecular radical recombination rate constant:

$$k = \frac{1}{4} \frac{k_d k_r}{k_d + k_r} = \frac{1}{4} \frac{k_d}{1 + \frac{k_d}{k_r}}. \quad (38)$$

When $\omega \rightarrow \infty$, which actually corresponds to the condition $\omega\tau_d \gg 1$, Eq. (23) is reduced to

$$k = \frac{k_d \frac{k_r}{4}}{k_d + \frac{k_r}{4} \left(1 + \frac{1}{1 + \sqrt{\tau_d/\tau_s}} \right)}. \quad (39)$$

This equation is identical to Eq. (27) describing the high-field result for $p_S^S + p_{T_0}^S = 1$. In high field S and T_0 are in equally populated. So, independent of how the reactivity is distributed over these two substates, they will exhibit an average reactivity of 0.5.

For the case of slow relaxation (applying for a number of spin-relaxation mechanism in high magnetic field) this expression may be simplified to give

$$k = \frac{1}{2} \frac{k_d \frac{k_r}{2}}{k_d + \frac{k_r}{2}}. \quad (40)$$

Result (40) was obtained earlier by Sarvarov and Salikhov [14] using the impact approximation.

5.3. The effect of electron spin relaxation and external magnetic field on the reaction rate constant

Let us first consider the effect of spin relaxation on the value of the reaction rate constant in zero field. For representing its parameter dependence in a conspicuous way it will be convenient to define the following two dimensionless parameters:

$$p = D/W_0\Delta R = \frac{k_d}{k_r}, \quad (41)$$

$$q = \tau_s W_0 \Delta / R; \quad (42)$$

of which p is simply the ratio of diffusion controlled and kinetic controlled reaction rate constant, while the parameter q measures the ratio of kinetic controlled rate constant and spin relaxation. In terms of p and q the rate constant in zero field (37) can be rewritten as

$$\zeta \equiv \frac{k}{k_d} = \frac{1 + \sqrt{pq}}{(1 + 4p)(1 + \sqrt{pq}) + 3\sqrt{pq}}. \quad (43)$$

A 3D plot of the dimensionless function $\zeta(p, q) \equiv k/k_d$ is shown in Fig. 2. The surface representing $\zeta(p, q)$ shows three limiting horizontal planes. (i) For both p and q small, meaning diffusion is slow and relaxation is fast relative to chemical reaction, $\zeta = 1$, i.e. the reaction is diffusion controlled. (ii) For p small, but q large, meaning that relaxation is slow in comparison to chemical reaction, $\zeta = 1/4$, i.e. only the radical pairs encountering as singlet radical pairs will react. (iii) For p large, i.e. diffusion is fast relative to chemical reaction, ζ tends to 0 because the reaction becomes kinetically controlled. The parameter q , i.e. spin relaxation, has no effect in this regime because the reaction probability per encounter is too small to perturb the spin equilibrium of the encounter radical pairs.

When inspecting Fig. 2 from the experimentalist's point of view one will be aware that variations along the p -axis can be achieved by changing the solvent viscosity and with it the diffusion coefficient. For small and large q the ζ variation as a function of p corresponds to single-step sigmoid curves representing the transition from diffusion controlled (with $\zeta = 1$ for small q , or $\zeta = 1/4$ for large q) to kinetic and spin statistics controlled ($\zeta \rightarrow 1/4p$). However, for intermediate values of q the sigmoid curves develop two steps wherein the transition from diffusion controlled to spin statistics and diffusion controlled and further to spin statistics and kinetically controlled become distinct. Systems corresponding to such q -sections would be particularly interesting to realize.

Let us now analyze the effect of an external magnetic field. With Eqs. (37) and (39) one obtains the following result for the maximum possible magnetic field effect η :

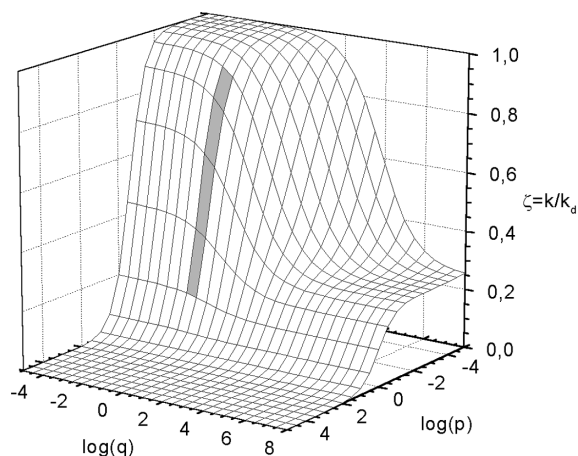


Fig. 2. 3D plot of the function $\zeta(p, q)$. For the series of mixed solvents investigated in Refs. [11,48] the p, q coordinates of the $\text{Ru}(\text{bpy})_3^{3+}/\text{MV}^{+\bullet}$ system fall within the marked grid elements.

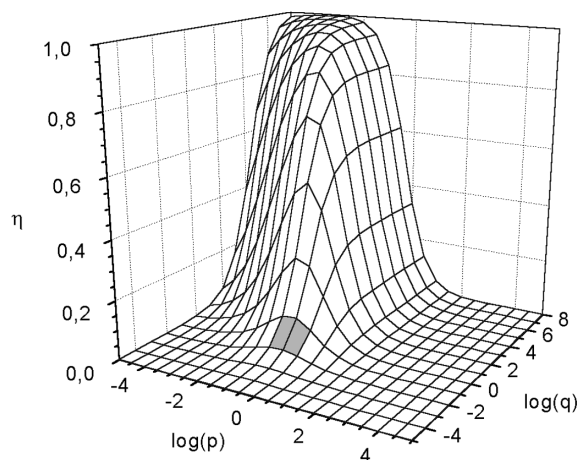


Fig. 3. 3D plot of the function $\eta(p, q)$. For aqueous solution the p, q coordinates of the $\text{Ru}(\text{bpy})_3^{3+}/\text{MV}^{+\bullet}$ system investigated in Ref. [47] fall within the marked grid elements.

$$\eta = \frac{k(\omega \rightarrow \infty)}{k(\omega = 0)} - 1 = \frac{\frac{k_r}{2k_d} \frac{1}{1 + \sqrt{\tau_d/\tau_s}}}{1 + \frac{k_r}{4k_d} \left(1 + \frac{1}{1 + \sqrt{\tau_d/\tau_s}}\right)} = \frac{2\sqrt{pq}}{1 + 4p + 2(1 + 2p)\sqrt{pq}}. \quad (44)$$

Fig. 3 illustrates relation (44). The field effect increases with q , i.e. with increasing relaxation time. This is due to the fact that spin relaxation anticipates the effect of magnetic field induced S–T conversion. Thus the magnetic field effect increases as spin relaxation becomes less efficient. On the other hand, the magnetic field effect is not, in general, a monotonic function of p . It is monotonic with p in the limiting case of large q . Here the field effect increases as diffusion, and with it the parameter p decreases. The maximum field effect reaches a plateau value of 1, corresponding to a doubling of the recombination rate constant. This corresponds to the case where radical pairs encountering with singlet spin recombine with efficiency 1 and where radical pairs encountering in the T_0 state undergo a complete T–S transition during one encounter. For finite q the field effect passes through a maximum on variation of p . The width of this maximum increases as q increases. The maximum in the p -dependence of the magnetic field effect η can be explained as follows: for small p , i.e. slow diffusion, the duration of the encounters is long enough that even slow relaxation can achieve effective T–S conversion so the magnetic field effect goes to zero as p goes to zero. For large p the diffusion is too fast, so that even for singlet encounters only a small fraction leads to reaction. Of course, in this case the spin equilibrium in the encounter pairs is not significantly perturbed by the reaction and the effect of an external magnetic field on an ensemble in spin equilibrium is zero.

5.4. Comparison with experimental results

The surfaces $\zeta(p, q)$ and $\eta(p, q)$ displayed in Figs. 2 and 3 may be considered as maps of landscapes wherein real experimental systems are to be located. Hence it is of interest to assign locations that have already been realized in experiments, so far, and to point out promising directions of future experimental investigations.

A reaction suitable to analyze in the light of the present theoretical results is the recombination of Ru(III)trisbipyridine ($\text{Ru}(\text{bpy})_3^{3+}$) with methylviologen radicals ($\text{MV}^{+\bullet}$), a reaction for which both geminate and homogeneous recombination have been studied in some detail [7–10,47,48].

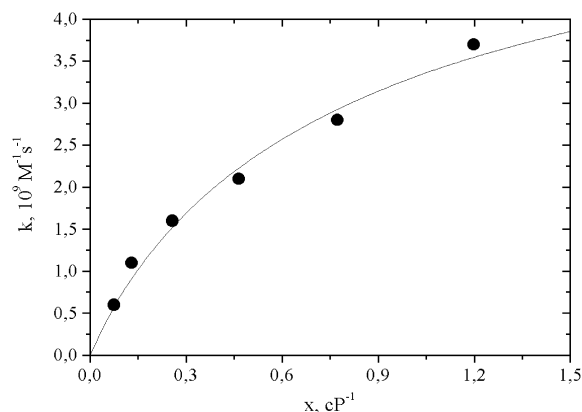


Fig. 4. Recombination rate constant k for bulk recombination of $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{MV}^{+\bullet}$ radicals as a function of inverse viscosity x . Data from Ref. [48]. Solid line: fit according to Eq. (37), cf. text.

The viscosity dependence of the second-order rate constant k of bulk recombination of $(\text{Ru}(\text{bpy})_3^{3+})$ and $\text{MV}^{+\bullet}$ radicals in a series of mixtures of water/acetonitrile (1:1) with ethylene glycol has been reported in Ref. [48]. The data plotted as a function of inverse viscosity are shown in Fig. 4. To assign values of k_d and k_r we fitted these data using Eq. (37) derived for the case $p_S^S = 1$ which should not be a too coarse approximation for this system ($p_S^S = 0.85$). The kinetic parameters k_d , k_r and τ_d are related to the molecular parameters D , ΔW_0 and R by the expressions:

$$k_d = 4\pi RD, \quad (45)$$

$$k_r = 4\pi R^2 \Delta W_0, \quad (46)$$

$$\tau_d = R^2/D. \quad (47)$$

The relative diffusion coefficient D of the two radical species was assumed to be a linear function of inverse viscosity x :

$$D = D_0 x/x_0, \quad (48)$$

where x_0 and D_0 are the corresponding values for the solvent of lowest viscosity. The following fixed values taken from Ref. [48] were used:

$$x_0 = 1.2 \text{ cP}^{-1}, \quad R = 10 \text{ \AA}, \quad \tau_s = 25 \text{ ps}.$$

The quantities D_0 and ΔW_0 were treated as free fit parameters in a least squares' fit of the kinetic data set. The parameters resulting from the fit are

$$D_0 = 1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1},$$

$$\Delta W_0 = 35 \text{ \AA ns}^{-1}.$$

The mere fact that the experimental data can be fitted by Eq. (37) must not be considered a proof that the radical recombination rate in this system is indeed affected by spin relaxation, nor is such a fit used to assign a value to τ_s . Fits of similar quality ensue when using the limiting forms of Eq. (37) for $\tau_s \rightarrow 0$ (Eq. (32)) or $\tau_s \rightarrow \infty$ (Eq. (38)). However, the values of the fit parameters, in particular of D (or else k_d) allow an

additional criterion to be applied. For the case $\tau_s \rightarrow 0$ the fit parameters are $D_0 = 1.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $\Delta W_0 = 29 \text{ \AA ns}^{-1}$, whereas in the case $\tau_s \rightarrow \infty$, $D_0 = 5.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $\Delta W_0 = 29 \text{ \AA ns}^{-1}$. On the other hand, values of $0.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $1.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ have been measured for the diffusion coefficients of $\text{Ru}(\text{bpy})_3^{2+}$ and MV^{2+} , respectively, in aqueous solution (0.89 cP at 25°C) [49]. Their sum of $1.51 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ probably represents a very good approximation to the value of the $\text{Ru}(\text{bpy})_3^{3+}/\text{MV}^{\bullet}$ pair. Comparing it with the kinetic fit value of D_0 given above, it is clear that a case of very short τ_s must apply. Of course, if we did not have independent experimental information that $\tau_s \approx 25$ ps from magnetic field effects on geminate cage escape [5,48] and from NMR measurements [50,51], it would not be possible to distinguish the cases $\tau_s \rightarrow 0$ ps and $\tau_s = 25$ ps on the basis of the D_0 fit-value alone. (Using the value of $p_S^S = 0.85$ together with Eq. (28) yields $D_0 = 1.44 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $\Delta W_0 = 33 \text{ \AA ns}^{-1}$, i.e. a result not significantly different from the values for $p_S^S = 1$). The value of $\approx 30 \text{ \AA ns}^{-1}$ obtained for $W_0 \Delta$ is rather independent of the τ_s value assumed for the kinetic fit. That this is a physically reasonable value can be judged from the value of W_0 that can be estimated from it. Assuming for the width of the reaction zone Δ a value of 1 \AA yields $W_0 \approx 30 \text{ ns}^{-1}$ which corresponds to a reaction time constant of about 30 ps for a $\text{Ru}(\text{bpy})_3^{3+}/\text{MV}^{\bullet}$ radical pair in contact, a value in the same order of magnitude as measured for chemically linked $\text{Ru}(\text{bpy})_3^{2+}\text{-MV}^{2+}$ dyads [52].

With the values of D and ΔW_0 determined, we are able to assign the $\{p, q\}$ range represented by the experimental data of the $\text{Ru}(\text{bpy})_3^{3+}/\text{MV}^{\bullet}$ system. For q , Eq. (42) yields a value of 0.087 that is independent of viscosity, while the values obtained for p from Eq. (41) vary between 0.44 and 0.028 over the range of viscosities probed in the experiments. The corresponding parameter range is marked on the $\zeta(p, q)$ surface shown in Fig. 2. This area is still in the zone where the kinetic behavior corresponds to the limit $\tau_s \rightarrow 0$ as was already apparent from the arguments presented above. Nevertheless, as Fig. 2 shows, the system is not too far from the interesting region where the spin relaxation kinetics is borne out in the viscosity dependence of the recombination rate constant. Such a borderline position of the system is also characteristic of the locus of our system on the $\eta(p, q)$ surface (cf. shaded area in Fig. 3): it appears that the representative area of the system is close to the rise of the ridge of the $\eta(p, q)$ surface. For the p, q values of 0.41 and 0.087, respectively, that we estimated for the $\text{Ru}(\text{bpy})_3^{3+}/\text{MV}^{\bullet}$ system in aqueous solution of 25°C, a theoretical magnetic field effect of 0.11 in the high field limit is obtained from Eq. (44). (If $p_S^S = 0.85$ is used the resulting magnetic field effect is 0.08.) Experimentally, the magnetic field effect on the rate constant of bulk recombination of $\text{Ru}(\text{bpy})_3^{3+}$ and MV^{\bullet} has been studied by Mukai et al. [47] who measured a saturation value of $\eta = 0.20 \pm 0.15$ at high fields. Our theoretical values are somewhat smaller, however, still in the limits of the accuracy of the experimental results, for which, unfortunately, the experimental error is very high. Therefore, a detailed fit of the field dependence did not seem worth while.

So far, the $\text{Ru}(\text{bpy})_3^{3+}/\text{MV}^{\bullet}$ system seems to be the only one for which experimental data of viscosity as well as magnetic field dependence of bulk recombination of radicals are available. As has been indicated in Figs. 2 and 3 the locus of this system on the $\zeta(p, q)$ and $\eta(p, q)$ surfaces are just at the border regions where spin and magnetic field effects become significant. A system perhaps suitable to shift the locus of the experimental system to higher q , meaning further into the spin controlled zone of the $\zeta(p, q)$ surface and up the ridge in the $\eta(p, q)$ surface is the 4-methoxybenzophenone ketyl/phenylthiyl radical pair ($\text{MBPH}^{\bullet}\text{PhS}^{\bullet}$) investigated by Wakasa et al. [53]. Although here the Δg value of ≈ 0.005 is much smaller than for the $\text{Ru}(\text{bpy})_3^{3+}/\text{MV}^{\bullet}$ pair, where the isotropic average of Δg is on the order of 0.5, it was shown that the magnetic field effect on the geminate radical escape in the $\text{MBPH}^{\bullet}\text{PhS}^{\bullet}$ system can still be driven into saturation at fields of some 10 T [53]. The spin relaxation time of the latter system is determined by the phenylthiyl radical of which it is said in Ref. [53] that it is “short”. Being an organic radical its spin relaxation time may be still by two or three orders of magnitude longer than for the $\text{Ru}(\text{bpy})_3^{3+}$ radical with its extremely short relaxation time of 25 ps. Thus the q -value of the $\text{MBPH}^{\bullet}\text{PhS}^{\bullet}$ pair might be two or three orders of magnitude larger than for the $\text{Ru}(\text{bpy})_3^{3+}/\text{MV}^{\bullet}$ pair and investigations of viscosity and magnetic field effects on the bulk recombination kinetics of the $\text{MBPH}^{\bullet}\text{PhS}^{\bullet}$ radicals might be a promising experiment

to do. With the stronger effects to be expected in this system it would perhaps be possible to verify the theoretical prediction that the magnetic field effect should pass over a maximum on proceeding to lower p , i.e. when increasing the viscosity of the solution. Furthermore, these experiments could even provide the value of the spin relaxation constant of the PhS^{*} radical that was not observable EPR spectroscopically in the experiments of Wakasa et al. [53].

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Appendix A

The impact approximation gives the following kinetic equation for the one-particle density matrix [16]:

$$\frac{d\sigma_A(t)}{dt} = i\hat{L}_A\sigma_A(t) - C_B^0 Tr_B \hat{P}\sigma_A(t) \otimes \sigma_B(t). \quad (\text{A.1})$$

Here σ_i ($i = A, B$) is one-particle density matrix averaged over an ensemble, \hat{L}_A is the Liouville super operator for particle A, C_B^0 is the initial concentration of particles B, \hat{P} is the impact operator,

$$\hat{P} = - \int \hat{W}(\vec{r}) \hat{G}(\vec{r}) d\vec{r}. \quad (\text{A.2})$$

Here $\hat{W}(\vec{r})$ is the distance dependent recombination operator, $\hat{G}(\vec{r})$ obeys equation

$$i[\hat{L}, \hat{G}(\vec{r})] + \hat{W}(\vec{r})\hat{G}(\vec{r}) + \hat{\mathcal{L}}(\vec{r})\hat{G}(\vec{r}) = 0 \quad (\text{A.3})$$

with boundary condition $\hat{G}(\vec{r}) \rightarrow \hat{E}$ at $r \rightarrow \infty$. Here $\hat{\mathcal{L}}(\vec{r})$ is the functional operator determined by the type of motion, \hat{E} is identity operator, \hat{L} is the Liouville super operator of RP, square brackets denote commutator $[x, y] = xy - yx$. If diffusional motion of non-charged particles is considered $\hat{\mathcal{L}}(\vec{r}) = D\nabla^2 = D\Delta$, D is the interdiffusion coefficient.

Let us now discuss the applicability of impact approximation to relaxing systems. We will consider here the most simple case when only relaxation is taken into account.

Let us first diagonalize matrix \hat{L} :

$$i\hat{L} = T\hat{\Lambda}T^{-1}. \quad (\text{A.4})$$

Here $A_{ik,lm} = \delta_{il}\delta_{km}\lambda_{ik}$, $\lambda_{ik} = \lambda_i^A + \lambda_k^B$, all $\lambda_{ik} \in \mathbb{R}$ and Eq. (A.3) may be rewritten as

$$(\lambda_{ik} - \lambda_{lm})\tilde{G}_{ik,lm}(\vec{r}) + \tilde{W}_{ik,ps}(\vec{r})\tilde{G}_{ps,lm}(\vec{r}) + \hat{\mathcal{L}}(\vec{r})\tilde{G}_{ik,lm}(\vec{r}) = 0, \quad (\text{A.5})$$

where $\tilde{W} = T^{-1}\hat{W}T$, $\tilde{G} = T^{-1}\hat{G}T$. Due to the contact character of recombination, the set of differential equations (A.5) may be reduced to the algebraic one:

$$\tilde{G}_{ik,lm}(R) - \delta_{il}\delta_{km} = \tilde{W}_{ik,ps}(R)\tilde{G}_{ps,lm}(R)f_{km}(R, R)\Delta, \quad (\text{A.6})$$

where Δ is reaction zone width, $f_{ik,lm}(r, r')$ is the Green's function of the equation

$$D\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}f_{ik,lm}(r, r') - (\lambda_{ik} - \lambda_{lm})f_{ik,lm}(r, r') = -\delta(r - r') \quad (\text{A.7})$$

with boundary conditions

$$f_{ik,lm}(r, r') \rightarrow 0, \quad r \rightarrow \infty,$$

$$\left. \frac{\partial}{\partial r} f_{ik,lm}(r, r') \right|_{r=R} = 0.$$

It should be noted that for $\lambda < 0$ the non-zero solution of the homogeneous equation

$$\begin{cases} D \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} v(r) - \lambda v(r) = 0, \\ v(r) \rightarrow 0, \quad r \rightarrow \infty, \\ \left. \frac{d}{dr} v(r) \right|_{r=R} = 0 \end{cases}$$

exists,

$$v = \frac{1}{r} \sin \sqrt{\tau_d |\lambda|} \left(\frac{r}{R} - 1 \right) + \frac{\sqrt{\tau_d |\lambda|}}{r} \cos \sqrt{\tau_d |\lambda|} \left(\frac{r}{R} - 1 \right),$$

so in this case we obtain a set of solutions of Eq. (A.6) which makes the value of $\tilde{G}_{ik,lm}(R)$ uncertain and therefore shows that the impact approximation is inapplicable.

Appendix B

Let us suppose as in Ref. [37] that at zero time $\sigma_{ik}^A(t=0) = n_A^{-1} \delta_{ik}$, $\sigma_{ps}^B(t=0) = n_B^{-1} \delta_{ps}$, $i, k = 1 \dots n_A$ and $p, s = 1 \dots n_B$ number one-particle states of radicals A and B respectively. One can see that for the Liouville operator obeying

$$\sum_{I,J,K} \hat{L}_{IJ,KK} = 0, \quad (\text{B.1})$$

where I, J, K correspond to the arbitrary two-particle basis, Eq. (1) conserve one-particle density matrices proportional to the unit matrix, i.e.

$$\begin{aligned} \sigma_{ik}^A(t) &= n_A^{-1} p_A(t) \delta_{ik}, \\ \sigma_{ps}^B(t) &= n_B^{-1} p_B(t) \delta_{ps}. \end{aligned} \quad (\text{B.2})$$

Here $p_A(t)$, $p_B(t)$ are survival probability for particles A and B, $p_A(t=0) = p_B(t=0) = 1$. Thus $C_{A,B}(t) = C_{A,B}^0 p_{A,B}(t)$ and

$$\frac{dp_A(t)}{dt} = C_B^0 n_A^{-1} n_B^{-1} \int_0^t m(\tau) p_A(t-\tau) p_B(t-\tau) d\tau, \quad (\text{B.3})$$

$$m(\tau) = \sum_{I,K} \hat{M}_{II,KK}(\tau), \quad (\text{B.4})$$

$$\tilde{m}(s) = s \sum_{I,P,S} \int \hat{W}_{II,PS}(\vec{r}) \tilde{\mathcal{P}}_{P,S}(\vec{r}, s) d\vec{r}. \quad (\text{B.5})$$

The pair density matrix $\mathcal{P}(\mathcal{P}_{IK} = \sum_N \hat{F}_{IK,NN})$ in the impact approximation obeys equation

$$\frac{\partial \mathcal{P}(\vec{r}, t)}{\partial t} = i \hat{L} \mathcal{P}(\vec{r}, t) + \hat{W}(\vec{r}) \mathcal{P}(\vec{r}, t) + \hat{\mathcal{L}}(\vec{r}) \mathcal{P}(\vec{r}, t) \quad (\text{B.6})$$

with initial condition $\mathcal{P}_{IK}(\vec{r}, t = 0) = \delta_{IK}$. And for the concentrations one derives the kinetic equation

$$\frac{dC_A(t)}{dt} = n_A^{-1} n_B^{-1} \int_0^t m(\tau) C_A(t - \tau) C_B(t - \tau) d\tau. \quad (\text{B.7})$$

Let us now consider the case when for radical B probabilities $W_{\alpha \rightarrow \beta}$ and $W_{\beta \rightarrow \alpha}$ of the relaxation transitions $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ are not equal, thus the condition (B.1) is not satisfied. Let $T_1 = T_2 = \tau_s$, $W_{\alpha \rightarrow \beta} + W_{\beta \rightarrow \alpha} = 1/\tau_s$, $W_{\alpha \rightarrow \beta}/W_{\beta \rightarrow \alpha} = \chi$. In this case relaxation operator of radical B takes the form:

$$\hat{Q}_B = \begin{bmatrix} -W_{\alpha \rightarrow \beta} & W_{\beta \rightarrow \alpha} & 0 & 0 \\ W_{\alpha \rightarrow \beta} & -W_{\beta \rightarrow \alpha} & 0 & 0 \\ 0 & 0 & -\frac{1}{\tau_s} & 0 \\ 0 & 0 & 0 & -\frac{1}{\tau_s} \end{bmatrix}, \quad (\text{B.8})$$

$$\hat{g}(s) = \begin{bmatrix} G & 0 & 0 & 0 \\ 0 & G & 0 & 0 \\ 0 & 0 & G & 0 \\ 0 & 0 & 0 & G \end{bmatrix}, \quad (\text{B.9})$$

$$G = \begin{bmatrix} \frac{g(s)+g(s+1/\tau_s)\chi}{1+\chi} & \frac{g(s)-g(s+1/\tau_s)}{1+\chi} & 0 & 0 \\ \frac{(g(s)-g(s+1/\tau_s))\chi}{1+\chi} & \frac{g(s)\chi+g(s+1/\tau_s)}{1+\chi} & 0 & 0 \\ 0 & 0 & g(s+1/\tau_s) & 0 \\ 0 & 0 & 0 & g(s+1/\tau_s) \end{bmatrix}. \quad (\text{B.10})$$

For the general case, the function $g(s)$ is defined by Eqs. (9) and (10), and for free continuous diffusion of non-charged particles by Eq. (11).

When initially non-correlated spin states are considered one can see that zero phase elements are conserved. For the $N = C_A^0(\sigma_1^A + \sigma_2^A) = C_B^0(\sigma_1^B + \sigma_2^B)$, $\Delta_A = C_A^0(\sigma_1^A - \sigma_2^A)$, $\Delta_B = C_B^0(\sigma_1^B - \sigma_2^B)$ one can get the following equations:

$$\frac{dN(t)}{dt} = \int_0^t ((\Delta_A \Delta_B - N^2)m_1 + N(\Delta_B - \Delta_A)m_2) d\tau, \quad (\text{B.11})$$

$$\frac{d\Delta_A(t)}{dt} = \int_0^t ((\Delta_A \Delta_B - N^2)m_2 + N(\Delta_B - \Delta_A)m_3) d\tau, \quad (\text{B.12})$$

$$\frac{d\Delta_B(t)}{dt} = \int_0^t ((\Delta_A \Delta_B - N^2)m_2 - N(\Delta_B - \Delta_A)m_3) d\tau + \left(N \frac{1-\chi}{1+\chi} - \Delta_B \right) \frac{1}{\tau_s}. \quad (\text{B.13})$$

For brevity, the time coordinate is omitted. All m_i under integral are taken in the time $t - \tau$, while N , Δ_A , Δ_B under integral are taken in the moment τ .

$$\tilde{m}_1(s) = \frac{k_r}{4R} (1 + z(s) + z(s + 1/\tau_s))(1 + \chi)^2, \quad (\text{B.14})$$

$$\tilde{m}_2(s) = \frac{k_r}{4R} (z(s) - z(s + 1/\tau_s))(1 - \chi^2), \quad (\text{B.15})$$

$$\tilde{m}_3(s) = \frac{k_r}{4R} (1 + z(s) + 3z(s + 1/\tau_s))(1 + \chi)^2, \quad (\text{B.16})$$

$$\begin{aligned}
R = & 1 + 4z(s + 1/\tau_s) + 2z^2(s + 1/\tau_s) + 2z(s) + 6z(s + 1/\tau_s)z(s) + (2 + 8z(s + 1/\tau_s) + 8z^2(s + 1/\tau_s) \\
& + 4z(s) + 4z(s + 1/\tau_s)z(s) + 4z^2(s))\chi + (1 + 4z(s + 1/\tau_s) + 2z^2(s + 1/\tau_s) + 2z(s) \\
& + 6z(s + 1/\tau_s)z(s))\chi^2,
\end{aligned} \tag{B.17}$$

$$z(s) = \frac{W_0}{4}g(s). \tag{B.18}$$

The symbol W_0 denotes the contact reaction probability per unit time. For the case of continuous diffusion (see Eq. (11)):

$$z(s) = \frac{W_0}{4} \frac{\tau_e}{1 + \sqrt{s\tau_d}} = \frac{1}{4} \frac{k_r}{k_d} \frac{1}{1 + \sqrt{s\tau_d}} \tag{B.19}$$

with $k_r = 4\pi R^2 \Delta W_0$.

It can be seen that for the $\chi \neq 1$ non-zero Δ_A and Δ_B appear as the spin system evolves in time.

Appendix C

Eq. (8) with Liouville operator (16) yields the following expression for $\hat{g}(s)$ in factorized basis:

$$\hat{g}(s) = \begin{bmatrix} G_1 & 0 & 0 & 0 \\ 0 & G_1 & 0 & 0 \\ 0 & 0 & G_2 & 0 \\ 0 & 0 & 0 & G_3 \end{bmatrix}, \tag{C.1}$$

$$G_i = \begin{bmatrix} x_1^i & x_2^i & 0 & 0 \\ x_2^i & x_1^i & 0 & 0 \\ 0 & 0 & x_3^i & 0 \\ 0 & 0 & 0 & x_4^i \end{bmatrix}, \quad i = 1, 2, 3. \tag{C.2}$$

Here

$$x_1^1 = \frac{1}{2}(g(s) + g(s + 1/\tau_s)); \tag{C.3}$$

$$x_2^1 = \frac{1}{2}(g(s) - g(s + 1/\tau_s)); \tag{C.4}$$

$$x_3^1 = g(s - ig_B\beta H + 1/\tau_s); \tag{C.5}$$

$$x_4^1 = g(s + ig_B\beta H + 1/\tau_s); \tag{C.6}$$

$$x_1^2 = \frac{1}{2}(g(s - ig_A\beta H) + g(s - ig_A\beta H + 1/\tau_s)); \tag{C.7}$$

$$x_2^2 = \frac{1}{2}(g(s - ig_A\beta H) - g(s - ig_A\beta H + 1/\tau_s)); \tag{C.8}$$

$$x_3^2 = g(s - i(g_A + g_B)\beta H + 1/\tau_s); \tag{C.9}$$

$$x_4^2 = g(s - i(g_A - g_B)\beta H + 1/\tau_s); \tag{C.10}$$

$$x_1^3 = \frac{1}{2}(g(s + ig_A\beta H) + g(s + ig_A\beta H + 1/\tau_s)); \quad (\text{C.11})$$

$$x_2^3 = \frac{1}{2}(g(s + ig_A\beta H) - g(s + ig_A\beta H + 1/\tau_s)); \quad (\text{C.12})$$

$$x_3^3 = g(s + i(g_A - g_B)\beta H + 1/\tau_s); \quad (\text{C.13})$$

$$x_4^3 = g(s + i(g_A + g_B)\beta H + 1/\tau_s). \quad (\text{C.14})$$

Appendix D

Relations between wave functions gives the following relations between density matrices in S–T and factorized bases

$$\rho_{SS} = \frac{1}{2}(\sigma_{12} + \sigma_{21} - \sigma_{34} - \sigma_{43}); \quad \rho_{T_0T_0} = \frac{1}{2}(\sigma_{12} + \sigma_{21} + \sigma_{34} + \sigma_{43});$$

$$\rho_{ST_0} = \frac{1}{2}(\sigma_{12} - \sigma_{21} + \sigma_{34} - \sigma_{43}); \quad \rho_{T_0S} = \frac{1}{2}(\sigma_{12} - \sigma_{21} - \sigma_{34} + \sigma_{43});$$

$$\rho_{ST_+} = \frac{1}{\sqrt{2}}(\sigma_{14} - \sigma_{41}); \quad \rho_{T_+S} = \frac{1}{\sqrt{2}}(\sigma_{13} - \sigma_{31});$$

$$\rho_{T_0T_+} = \frac{1}{\sqrt{2}}(\sigma_{14} + \sigma_{41}); \quad \rho_{T_+T_0} = \frac{1}{\sqrt{2}}(\sigma_{13} + \sigma_{31});$$

$$\rho_{ST_-} = \frac{1}{\sqrt{2}}(\sigma_{32} - \sigma_{23}); \quad \rho_{T_-S} = \frac{1}{\sqrt{2}}(\sigma_{42} - \sigma_{24});$$

$$\rho_{T_0T_-} = \frac{1}{\sqrt{2}}(\sigma_{32} + \sigma_{23}); \quad \rho_{T_-T_0} = \frac{1}{\sqrt{2}}(\sigma_{42} + \sigma_{24});$$

$$\rho_{T_+T_+} = \sigma_{11}; \quad \rho_{T_-T_-} = \sigma_{22}; \quad \rho_{T_+T_-} = \sigma_{33}; \quad \rho_{T_-T_+} = \sigma_{44}.$$

And the inverse relations

$$\sigma_{11} = \rho_{T_+T_+}; \quad \sigma_{22} = \rho_{T_-T_-}; \quad \sigma_{33} = \rho_{T_+T_-}; \quad \sigma_{44} = \rho_{T_-T_+};$$

$$\sigma_{12} = \frac{1}{2}(\rho_{SS} + \rho_{ST_0} + \rho_{T_0S} + \rho_{T_0T_0}); \quad \sigma_{21} = \frac{1}{2}(\rho_{SS} - \rho_{ST_0} - \rho_{T_0S} + \rho_{T_0T_0});$$

$$\sigma_{13} = \frac{1}{\sqrt{2}}(\rho_{T_+S} + \rho_{T_+T_0}); \quad \sigma_{31} = \frac{1}{\sqrt{2}}(-\rho_{T_+S} + \rho_{T_+T_0});$$

$$\sigma_{14} = \frac{1}{\sqrt{2}}(\rho_{ST_+} + \rho_{T_0T_+}); \quad \sigma_{41} = \frac{1}{\sqrt{2}}(-\rho_{ST_+} + \rho_{T_0T_+});$$

$$\sigma_{23} = \frac{1}{\sqrt{2}}(-\rho_{ST_-} + \rho_{T_0T_-}); \quad \sigma_{32} = \frac{1}{\sqrt{2}}(\rho_{ST_-} + \rho_{T_0T_-});$$

$$\sigma_{24} = \frac{1}{\sqrt{2}}(-\rho_{T_-S} + \rho_{T_-T_0}); \quad \sigma_{42} = \frac{1}{\sqrt{2}}(\rho_{T_-S} + \rho_{T_-T_0});$$

$$\sigma_{34} = \frac{1}{2}(-\rho_{SS} + \rho_{ST_0} - \rho_{T_0S} + \rho_{T_0T_0}); \quad \sigma_{43} = \frac{1}{2}(-\rho_{SS} - \rho_{ST_0} + \rho_{T_0S} + \rho_{T_0T_0}).$$

Using these relations one can get expressions for non-zero elements of recombination operator represented in Tables 1 and 2.

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