Temperature dependence of the singlet—triplet (S—T$_0$) transitions in strong magnetic fields

L. VALKO

Department of Physical Chemistry, Faculty of Chemical Technology, Slovak Technical University, CS-812 37 Bratislava

Dedicated to Academician V Kellö, in honour of his 70th birthday

Temperature effect on the S—T$_0$ transitions in the radical pairs is studied. From the derived equations it follows that the temperature effect significantly influences an oscillation of the radical pair spin state between singlet and triplet. The effect of spin polarization component and relaxation process due to Brownian rotational diffusion of radical pair is examined. The rotational relaxation process may affect the decay rate of spin polarization by providing an alternate means of orienting magnetic dipoles of radical pair components.

Изучено влияние температуры на S—T$_0$ переходы в радикальных парах. Из производных уравнений следует, что температура оказывает значительное влияние на осцилляцию спинового состояния радикальной пары между синглетным и триплетным. Исследован эффект компонента спиновой поляризации и релаксационного процесса, возникающего вследствие брауновской вращательной диффузии радикальной пары. Процесс вращательной релаксации может воздействовать на скорость затухания спиновой поляризации вследствие предоставления альтернативных способов ориентировки магнитных диполей компонентов радикальной пары.

Studies of external magnetic field effects upon intramolecular and intermolecular dynamical processes have recently made much progress. New phenomena have been observed concerning intramolecular and intermolecular energy transfer [1, 2], chemical reactions [3—10], and also their mechanisms have been clarified for some cases. The intramolecular phenomena include the magnetic field effects on radiative [11] and nonradiative [12] decay processes, and the reactivity of triplet states [13]. The intermolecular phenomena are related with the selection rule of reactions induced by the collision of excited molecules or radicals with some spin multiplicities. It can be already concluded that the magnetic field effect on chemical reactions is useful not only for the determination of the reaction mechanism but also for the control of the product yields, *e.g.* in the case of photochemical reactions [14].

The essential feature of the radical pair mechanism of chemically induced nuclear and electron spin polarization is mixing of the reactive singlet and unreactive triplet electron spin states of the radical pair by the electron—nuclear hyperfine interactions within the individual radicals [15]. We confine ourselves here only to the chemical transformations occurring in large magnetic fields. In these fields, however, it is generally assumed that only mixing of the singlet (S) and triplet (T_0) states need to be considered, because the large Zeeman splitting of the $T_{\pm 1}$ states severely limits their being mixed with the S and T_0 states by hyperfine interactions of typical magnitude. Many problems, however, are still left unsolved in this field. For example, the temperature magnetic field effect upon chemical reactions may be expected to be fruitful research to be developed. The aim of this paper is to develop the theory for the temperature effect on the S—T_0 transitions in radical pairs which are generated in a singlet spin state from the singlet precursor. In reality, various S—T_0 transition rates may correspond to various states of the radical pair in contact, *e.g.* different conformations or mutual orientations of the radicals. The present paper is an attempt to take into account, at least roughly, the above circumstances without mathematical complications.

Thermodynamic approach

What is the rate-determining step for formation and decay of a singlet radical pair? This is now a fundamental question in radical chemistry in the presence
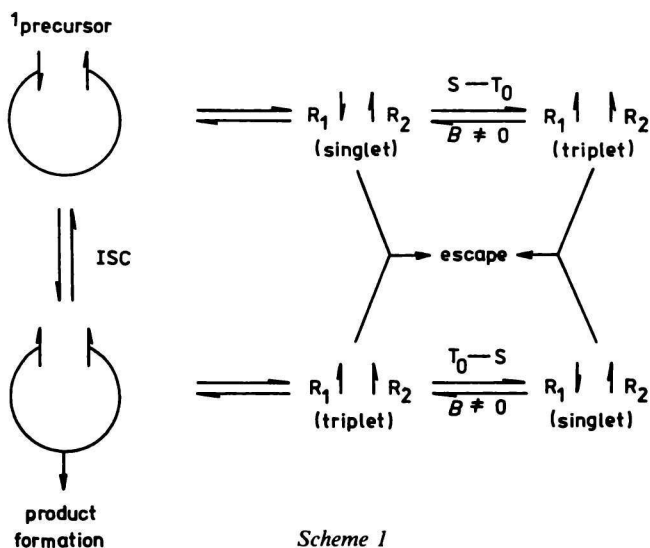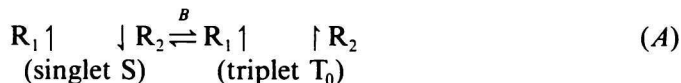

Scheme 1

of the external magnetic field and the answer is expected to depend in some way on the radical pair structure and on experimental conditions. In principle, the rate-determining step could be any one of the four processes shown in Scheme 1: *1.* Intersystem crossing (ISC) to the triplet biradical; *2.* interconversion among radical pair conformers (occurring in both singlet and triplet); *3.* product formation from a singlet radical pair in a conformer poised for product formation; *4.* escape products formation (occurring in both singlet and triplet) (Scheme 1).

In the thermal reactions the precursor is usually a diamagnetic (singlet state) molecule. In photochemical reactions both singlet and triplet state precursors may occur. Alternatively, radical pair formation may occur by random encounters of free radicals (F pairs). We confine our attention here only to the interconversion among radical pair conformers.

Let us consider the equilibrium between singlet S and triplet T_0 states as described by

$$\underset{\text{(singlet S)}}{R_1\uparrow\quad\downarrow R_2}\overset{B}{\rightleftharpoons}\underset{\text{(triplet }T_0)}{R_1\uparrow\quad\uparrow R_2} \qquad (A)$$

where B is the induction of external magnetic field. The apparent equilibrium constant for "reaction" (A) is defined as

$$K = \frac{[\text{triplet}]}{[\text{singlet}]} = \frac{f_{T_0}}{f_S} = \frac{f_{T_0}}{1 - f_{T_0}} \qquad (1)$$

where f_{T_0} is the fraction of radical pairs in the triplet T_0 state at equilibrium. It can be concluded that an external magnetic field enhances the singlet—triplet mixing of radical pairs in solutions through the electronic Zeeman term due to difference in the g factors between the two-component radicals and reduces the mixing through the hyperfine coupling term.

From the well-known Van't Hoff equation, one obtains

$$\left(\frac{\partial(\ln K)}{\partial T}\right)_{p,B} = \frac{1}{f_{T_0}(1 - f_{T_0})}\frac{df_{T_0}}{dT} = \frac{\Delta E_{T_0 S}}{k_B T^2} \qquad (2)$$

where $\Delta E_{T_0 S} = E_{T_0} - E_S$ is energy change (per radical pair) going from the singlet to triplet state. The interaction energy between the two radicals R_1 and R_2 is relatively well approximated by the exchange interaction $J(r)$. It is reasonable, following *Adrian* [16], to approximate this short range function as

$$J(r) = \frac{1}{2}(E_S - E_{T_0}) = J_0 e^{-\lambda r}, \quad J_0 < 0 \qquad (3)$$

where the sign of J_0 is chosen so that the singlet is lower in energy than the triplet, the case is illustrated in Fig. 1, as well as the usual case for a radical pair which can recombine by covalent bond formation. $J(r)$ depends on the overlap of the nonbonded electron charge clouds around the interacting radicals.
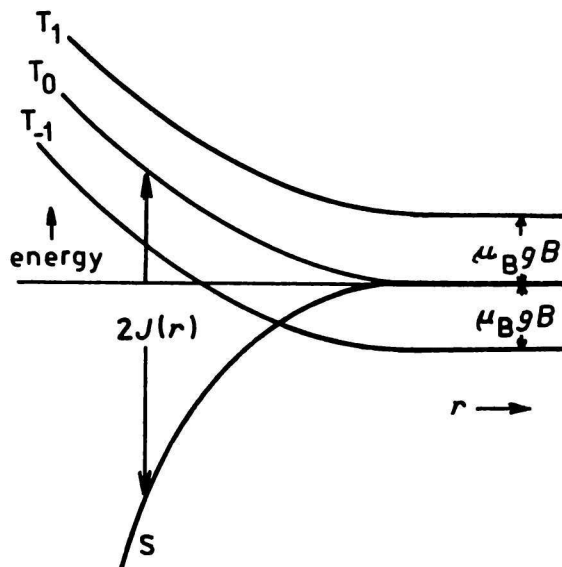

Fig. 1. Singlet and triplet energy levels of a radical pair in an external magnetic field as a function of separation.

Therefore, we identify $\Delta E_{T_0 S} = 2|J(r)|$. It already has been shown that the S—T_0 conversion in a radical pair in solution is affected by an external field while the energy separation between the singlet and triplet ground state, $2J(r)$, is the exchange interaction comparable with, or smaller than the difference between the Zeeman energies of the component radicals or their hyperfine energies [17]. When radical pair is formed from an S precursor it will initially also be in the singlet state ($R_1 \uparrow \downarrow R_2$ — antiparallel spins). The radicals of the spin will separate by diffusion and the mutual exchange interaction $J(r)$ decreases. $J(r)$ (or $\Delta E_{T_0 S} = 0$) will eventually vanish and S and T_0 states (triplet state with $M_S = 0$) are almost degenerate (Fig. 1). From this it follows that quantitative evaluation of the equilibrium constant (*1*) and the other thermodynamic parameters for S—T_0 equilibrium (*A*) involving radical pair polarization, according to the Van't Hoff equation (*2*) is not adequate. However, realization of this intention under suitable conditions for a range of solvents and temperatures is very desirable. Therefore we choose another approach to solve the problem.

Singlet (S)—triplet (T_0) mixing

The process of S—T_0 interconversion is easily envisaged in the vector representation shown in Fig. 2. The electrons on both radicals precess about the strong magnetic field direction and with a well-defined phase relationship, which causes the two vectors to lie in the same plane. The singlet S state $|S\rangle = 2^{-\frac{1}{2}}|(\alpha\beta - \beta\alpha)\rangle$ is by definition a state with zero angular momentum and is therefore represented by a pair of vectors pointing in opposite directions. In the T_0 state $|T_0\rangle = 2^{-\frac{1}{2}}|(\alpha\beta + \beta\alpha)\rangle$ (where $\alpha\beta$ implies that radical 1 has α electron spin and radical 2 has β electron spin, and conversely for radical 2) the vectors are in phase although the resultant projection in field direction (along the z axis) is zero (hence the label T_0), but they have net angular momentum — a nonzero projection in the perpendicular directions (in xy plane). To accomplish the transition of a radical pair in the S state to T_0 it is necessary to cause one of the vectors to precess at a greater rate than the other. After the radicals separate to a point where the electron—spin-dependent exchange interaction is negligible ($J(r) = 0$), each spin will precess independently about its own effective magnetic field. The condition for S—T_0 mixing is simply that this local field differs at the two electrons. The difference in precession frequences for particular electrons can be found in [17].
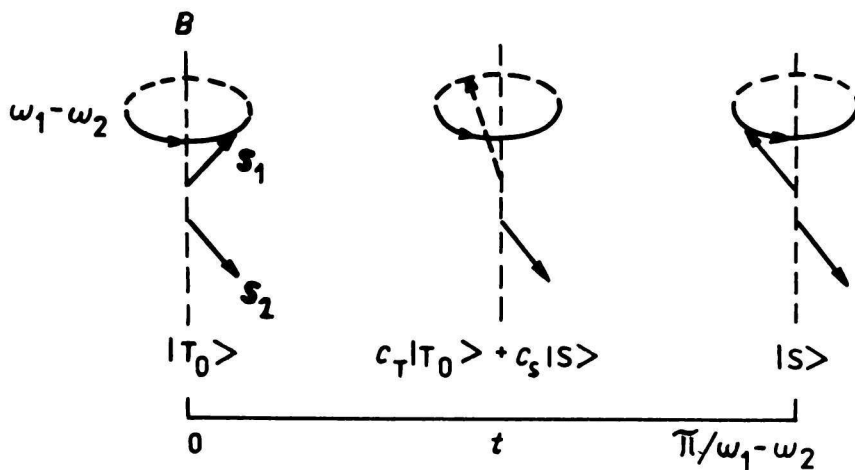

Fig. 2. Vector diagram of singlet (S)—triplet (T_0) mixing. At time $t = 0$ the vector sum of the spins of the two unpaired electrons is zero. S_1 precesses around the magnetic field B with angular frequency ω_1, S_2 with ω_2. Depicted is the phase relation between S_1 and S_2 as a function of t, keeping S_2 fixed and having S_1 precess with the difference frequency.

155

Dynamics of the S—T_0 transition

According to the vector model, the S—T_0 transitions are accompanied with periodic transitions between the two vector configurations shown in Fig. 2. It is known that S—T_0 mixing is a slow process and the radical pair must separate before it becomes singlet and is consumed by reaction. There is consequently a probability that the members of this original pair will reencounter at a later time. If they are able to, they react but otherwise they experience the strong exchange interaction at this collision before separating once more. This situation differs from that in which the pair was first created in that it now has a mixed $|S\rangle$ and $|T_0\rangle$ character, rather than the original pure S state. Assuming the rapid S—T_0 transitions between the two states depending on the magnetic field and temperature, the averaged angular frequency of precession between the two states is (Fig. 2)

$$\bar{\omega}_{T_0 S} = f_S \omega_S + f_{T_0} \omega_{T_0} = \omega_S + (\omega_{T_0} - \omega_S) f_{T_0} \tag{4}$$

where f_S is the fractional population of the S spin state of radical pair with the angular frequency ω_S, and $f_{T_0} = 1 - f_S$ is the fractional population of the T_0 state of radical pair with the angular frequency ω_{T_0}. The parameters f_S (f_{T_0}), ω_S, ω_{T_0} refer to the temperature of measurement. If it can be assumed that ω_S and ω_{T_0} are independent of temperature (and are therefore given by room temperature data) then f_S (or f_{T_0}) can be determined, but the procedure can be subjected to some errors.

The fractional populations, with respect to eqn (1), are related as

$$f_{T_0}/f_S = \exp(-\Delta G^\circ/k_B T) \tag{5}$$

whence

$$f_{T_0} = (1 - f_{T_0}) \exp(-\Delta G^\circ/k_B T) = K/(1 + K) = [\exp(\Delta G^\circ/k_B T) + 1]^{-1} \tag{6}$$

where ΔG° is the standard free-energy change of the reaction (A) which is related to the equilibrium constant K through the relation $\Delta G^\circ = -k_B T \ln K$.

We have already mentioned that after the radicals separate to a point where electron—spin-dependent exchange interaction is negligible, each spin will precess independently about its own effective magnetic field. The condition for S—T_0 mixing is simply that this local field differs at the two electrons in both spin states, e.g. S and T_0, and we use the symbol ω, to denote this difference. Let

$$\omega = \omega_{T_0} - \omega_S \tag{7}$$

where ω is less than the Zeeman splitting (Fig. 1) and also than the exchange interaction $J(r)$ at short distances, and can affect the development of the radical

156

pair only when the radicals have separated to a point where S and T_0 are almost degenerate. Then, eqn (5) can be written in the form

$$\bar{\omega}_{T_0 S} = \omega_S + \omega f_{T_0} \tag{8}$$

from which it follows that $\bar{\omega}_{T_0 S} = \omega_S$ for $f_{T_0} = 0$ and $\bar{\omega}_{T_0 S} = \omega_S + \omega$ for $f_{T_0} = 1$.

Temperature effect on the S—T_0 mixing

Substituting expression (6) for f_{T_0} into eqn (8) and differentiating with respect to $1/T$ gives (if $\Delta G°$ is temperature-independent)

$$\frac{d(\bar{\omega}_{T_0 S} - \omega_S)}{d(1/T)} = \left\{ \frac{d\omega}{d(1/T)} - \frac{\omega \Delta G°}{k_B} \frac{\exp(\Delta G°/k_B T)}{1 + \exp(\Delta G°/k_B T)} \right\} \cdot$$
$$\cdot [1 + \exp(\Delta G°/k_B T)]^{-1} \tag{9}$$

from which it follows that the process of S—T_0 interconversion is temperature-dependent. Taking into account $\Delta G° = \Delta H° - T\Delta S°$ (where $\Delta H°$ is the standard enthalpy change, $\Delta E° = \Delta E_{T_0 S}$, and $\Delta S°$ is the standard entropy change), we can see that $\Delta G°$ is surely different from zero ($\Delta G° \neq 0$), and it is in that case if $\Delta E_{T_0 S} = 0$, because certainly already the alone S—T_0 entropy contribution $\Delta S° \neq \Delta S_{T_0 S} \neq 0$. However, besides S—$T_0$ entropy contribution one should consider other entropy contributions (*e.g.* at least the entropy contribution for translation, free rotation, and hindered rotation of radical pair).

We admit situation when a zero value of $\Delta G°$ can result from the same absolute magnitude of $\Delta E_{T_0 S}$ and $T\Delta S°_{ST_0}$, *e.g.* $\Delta E_{T_0 S} = T\Delta S°_{T_0 S}$, this is the so-called compensation effect. Thus, for $\Delta G° = 0$, from eqn (9) we have

$$\bar{\omega}_{T_0 S} - \omega_S - \omega = \text{const} \tag{10a}$$

or

$$\bar{\omega}_{T_0 S} - \omega_S = \text{const} + \omega = \omega' \tag{10b}$$

from which it follows that the process of S—T_0 interconversion is parametrically temperature-dependent. However, S—T_0 transition under such condition is little probable.

Since $K = \exp(-\Delta G°/k_B T)$, we rearrange eqn (9)

$$\frac{d(\bar{\omega}_{T_0 S} - \omega_S)}{d(1/T)} = \left\{ \frac{d\omega}{d(1/T)} - \frac{\omega \Delta G°}{k_B} \frac{1}{1 + K} \right\} \frac{K}{1 + K} \tag{11}$$

Now, consider the two special cases. If $\Delta G° \gg 0$, then $K \ll 1$,

and

$$\frac{d(\bar{\omega}_{T_0 S} - \omega_S)}{d(1/T)} = \left(\frac{d\omega}{d(1/T)} - \frac{\omega \Delta G^\circ}{k_B}\right) K \tag{12}$$

and if $|d\omega/d(1/T)| \ll |\omega \Delta G^\circ/k_B|$, then we obtain

$$\frac{d(\bar{\omega}_{T_0 S} - \omega_S)}{d(1/T)} = -K \frac{\omega \Delta G^\circ}{k_B} \tag{13}$$

and on the contrary, if $|d\omega/d(1/T)| \gg |\Delta G^\circ/k_B|$, then

$$\frac{d(\bar{\omega}_{T_0 S} - \omega_S)}{d(1/T)} = K \frac{d\omega}{d(1/T)} \tag{14}$$

or

$$\frac{d(\bar{\omega}_{T_0 S} - \omega_S - K\omega)}{d(1/T)} = -\omega \frac{dK}{d(1/T)} = \omega K \frac{\Delta G^\circ}{k_B} \tag{15}$$

since $d(K\omega)/d(1/T) = \omega \, dK/d(1/T) + K \, d\omega/d(1/T)$.
On the other hand, if $\Delta G^\circ \ll 0$, then $K \gg 1$, and

$$\frac{d(\bar{\omega}_{T_0 S} - \omega_S)}{d(1/T)} = \frac{d\omega}{d(1/T)} - \frac{\omega \Delta G^\circ}{k_B K} \tag{16}$$

and if now $|d\omega/d(1/T)| \gg |\omega \Delta G^\circ/(k_B K)|$, then

$$\bar{\omega}_{T_0 S} - \omega_S = \omega'$$

And on the contrary, if $|d\omega/d(1/T)| \ll |\omega \Delta G^\circ/(k_B K)|$, then

$$\frac{d(\bar{\omega}_{T_0 S} - \omega_S)}{d(1/T)} = -\frac{\omega \Delta G^\circ}{k_B K} \tag{17}$$

If the temperature coefficients $d\bar{\omega}_{T_0 S}/d(1/T)$ and $d\omega_S/d(1/T)$ are of like and approximately the same magnitude, e.g. $\bar{\omega}_{T_0 S} = \omega_S$, or in other words, if we identify $\bar{\omega}_{T_0 S}$ with ω_S, then from eqn (9) it follows

$$\frac{d(\ln \omega)}{d(1/T)} = \frac{\Delta G^\circ}{k_B(1 + K)} \tag{18}$$

If now $K \ll 1$, then

$$\frac{d(\ln \omega)}{d(1/T)} = \frac{\Delta G^\circ}{k_B} \tag{19}$$

and if $K \gg 1$

$$\frac{d(\ln \omega)}{d(1/T)} = \frac{\Delta G^\circ}{k_B K} \tag{20}$$

From the derived equations it follows that the temperature effect significantly influences an oscillation of the electron spin system (radical pair) between the $|S\rangle$ state, where the two electron spins are antiparallel, and $|T_0\rangle$ state where the projection of the two spins along B is zero but is maximized along an axis perpendicular to B (Fig. 2). The period of this oscillation is $2\pi/\omega$, *i.e.* the lifetime of the radical pair as an entity before it either undergoes cage reaction or separates completely (Scheme 1). Thus an initial $|S\rangle$ state, which we have accepted in derivation of eqns (*18—20*) which are similar to the Van't Hoff equation (*2*), will evolve in time π/ω into a pure $|T_0\rangle$ state, with a mixture of $|T_0\rangle$ and $|S\rangle$ states.

The period of this oscillation of a radical pair in solution, and the other dynamical parameters (*e.g.* $\bar{\omega}_{T_0S}$, ω_S) measurable in principle, may be obtained from the time dependence of the electron spin resonance spectrum of the radical pair produced in a spin-polarized state by chemical reaction (Scheme 1). However, electron relaxation in normal liquids is fast and can be measured only by using a rapid-response ESR spectrometer [18]. From this it follows that quantitative evaluations of the equilibrium constant and the other thermodynamic parameters for the equilibrium (*A*) involving radical pair polarization must be performed in a short time compared with observation time. Under suitable conditions the time dependence is exponential and occurs with an effective spin-lattice time which depends on the true relaxation process investigated for a range of solvents and temperatures. It seems that S—T_0 transition is a sensitive function of the viscosity of the medium and rises sharply as the viscosity falls. If this phenomenon is genuinely unimolecular, one is forced to the conclusion that the S—T_0 transition must arise (besides the structural characteristics of radical pair) from the purely mechanical motion of the medium relative to the radical pair. On this hypothesis, one is led to consider the mechanical history of radical pair, and to regard the nonradiative energy S—T_0 transition as a transition reduced by a fluctuating mechanical perturbations, namely the time--dependent forces exerted on the radical pair by its neighbours. Now, there exists a simple connection between the fluctuating forces on a radical pair and its diffusion constant. Briefly, the diffusion constant is determined by the low--frequency components of the fluctuating force, and according to the Einstein theory of Brownian diffusion the viscosity is related to the diffusion constant by the known Einstein equation. We shall deal with this problem in the next section.

A simple rotational model process

As we have already mentioned S—T_0 mixing affects the reactivity of the radical pair, because recombination is possible only from the S state (Scheme 1),

and in principle the S—T_0 transitions are degenerate energetically but not entropically. The crucial point is now that the spin vectors of a radical pair precess with different angular rates about the direction of the magnetic field B and under such situation at various temperatures it is instructive to consider the fundamental contribution to relaxation process to be due to the spin-rotation interaction [19]. Emphasis will be on presenting a physical picture of the process rather than mathematical rigour. We lay stress here upon effects associated with the instantaneous orientation of the diffusing radical pair and the surrounding molecules which might lead to time-varying preferences for certain directions of rotational diffusional displacement.

For the sake of simplifying the mathematical effort, let us consider our model reaction (A) which is as uncomplicated as possible but nevertheless discloses clearly the basic aspects of our intention.

The unimolecular reaction process is

$$R_1 \downarrow \uparrow R_2 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} R_1 \uparrow \uparrow R_2 \qquad (A')$$

where k_{12} and k_{21} denote the rate constants for the forward and reverse reactions, respectively. They are related to the equilibrium concentrations S and T_0 and the equilibrium constant K by the well known relation

$$K = \frac{k_{12}}{k_{21}} = \frac{[T_0]}{[S]} \qquad B \neq 0 \qquad (21)$$

The crucial point is now that we ascribe the S—T_0 transition to the rotational diffusion of electron spin vectors S_1 and S_2 of a molecular radical rotational diffusion R_1 and R_2 of the radical pair which is associated with electron spin vectors S_1 and S_2. In the radical pair in state S an axis is defined by the direction of spin vectors S_1 and S_2. This axis is to be conserved for the S—T_0 transition (Fig. 3). Thus also an axis for the radical pair in particular state is introduced.
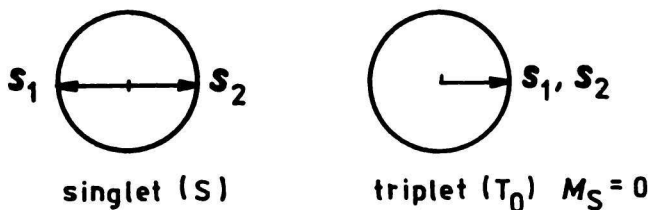

singlet (S)   **triplet (T_0) $M_S = 0$**

Fig. 3. Projections of electron spin vectors S_1 and S_2 of a radical pair in the xy plane perpendicular to the magnetic field direction for a singlet (S) and triplet (T_0) state.

Owing to fluctuating forces, there will be a distribution of the axes with respect to the direction of an applied magnetic field. For our rotational diffusion model of a radical pair, the rotational diffusion coefficient is given by the relation [20]

$$D_r = \int_0^\infty \langle \vartheta(0)\, \vartheta(t) \rangle \, dt = \langle \omega^2 \rangle \, \tau_j = \frac{k_B T}{I_r} \tau_j \tag{22}$$

where $\langle \omega^2 \rangle$ is the mean-square value of the angular velocity, τ_j is the correlation time for fluctuations in rotational angular momentum, and I_r is the reduced moment of inertia of radical pair defined as $I_r = I_1 I_2 / (I_1 + I_2)$, where I_1 and I_2 are the moments of inertia of radical pair components (R_1 and R_2).

The concentration of these radical pairs which have axes pointing at the time t into the solid angle $d\Omega = 2\pi \sin \vartheta \, d\vartheta$ (ϑ being the angle between B and a radical pair — rotation axis) can be expressed as

$$dc(S) = \Theta_S(\vartheta, t) \, d\Omega \quad dc(T_0) = \Theta_{T_0}(\vartheta, t) \, d\Omega$$

The distribution functions $\Theta_S(\vartheta, t)$ and $\Theta_{T_0}(\vartheta, t)$ in the meaning of the concentrations per solid angle may change owing to the different precessing rates of the spin vectors S_1 and S_2 which alternate between S and T_0 orientations (Fig. 2) and describe mixing of S and T_0 states, but also on account of rotational diffusion of radical pair. This is described by the two partial differential equations

$$\frac{\partial \Theta(S)}{\partial t} = -v_{12} + D_r \nabla^2 \Theta(S) \tag{23}$$

$$\frac{\partial \Theta(T_0)}{\partial t} = v_{12} + D_r \nabla^2 \Theta(T_0) \tag{24}$$

with $\Theta_S(\vartheta, t) \equiv \Theta(S)$ and $\Theta_{T_0}(\vartheta, t) \equiv \Theta(T_0)$. We have neglected here the moment of force exerted by the magnetic field. The effect of the reaction rate is represented by

$$v_{12} = -\left(\frac{\partial \Theta(S)}{\partial t} \right)_{spin} = \left(\frac{\partial \Theta(T_0)}{\partial t} \right)_{spin} =$$

$$= k_{12} \Theta(S) - k_{21} \Theta(T_0) = k_{21}(K\Theta(S) - \Theta(T_0)) \tag{25}$$

It should be emphasized that owing to the perturbation of the S—T_0 transition by the magnetic field the rate constants k_{12} and k_{21} as well as the corresponding equilibrium constant K depend on the induction of magnetic field B and ϑ. For $B = 0$ they are, of course, identical with k_{12}°, k_{21}° or K°, respectively.

The term $D_r\nabla^2\Theta_i$ $(i = S, T_0)$ in eqns (23) and (24) results from rotational diffusion taking into account the second Fick's law. Transforming the Laplace operator to spherical coordinates ∇^2 in our case yields

$$\nabla^2\Theta_i = \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left\{\sin\vartheta\frac{\partial\Theta_i}{\partial\vartheta}\right\} \qquad (26)$$

Fortunately it will not be necessary to find the general solution of eqns (23) and (24). Since $\mu B/k_B T \ll 1$, where μ is the representative magnetic moment (usually by orders of magnitude), the magnetic field causes only very slight deviations from the state corresponding to $B = 0$, i.e. random distribution of the radical pair axes with respect to the direction of an applied magnetic field. Following Kaptein's [21] line reasoning we set

$$\Theta(S) \approx \Theta(S)° + \frac{\mu B}{k_B T}\varphi_S(\vartheta,t) + \qquad (27)$$

$$\Theta(T_0) \approx \Theta(T_0)° + \frac{\mu B}{k_B T}\varphi_{T_0}(\vartheta,t) + \qquad (28)$$

where

$$\Theta(S)° = \frac{\langle c(S)°\rangle}{4\pi} \qquad \Theta(T_0)° = \frac{\langle c(T_0)°\rangle}{4\pi} \qquad (29)$$

and

$$K_0 = \frac{\Theta(T_0)°}{\Theta(S)°} = \frac{k_{12}°}{k_{21}°} \qquad (30)$$

Any term of second or higher order in the magnetic field will be neglected. Now, inserting eqns (27) and (28) into the rate term v_{12} with respect to (25) leads to

$$v_{12} = k_{12}\Theta(S)° - k_{21}\Theta(T_0)° + \frac{\mu B}{k_B T}(k_{12}\varphi_S(\vartheta, t) - k_{21}\varphi_{T_0}(\vartheta,t)) +$$

and after rearrangement of the first term with respect to eqns (29) and (30)

$$v_{12} = \frac{k_{12}k_{21}°}{k_{12}°}\Theta(T_0)°B\left(\frac{\partial(\ln K)}{\partial B}\right)_{T,p} + \frac{\mu B}{k_B T}(k_{12}\varphi_S(\vartheta,t) -$$

$$- k_{21}\varphi_{T_0}(\vartheta,t)) + \qquad (31)$$

where we denoted $K - K_0 = \delta K$.

Now, if ΔM represents the molar change of the over-all magnetic dipole moment M which is produced by reaction (A) (proceeding from the left to the right) while keeping the intensive variables T and p constant, then [22]

162

$$\left(\frac{\partial(\ln K)}{\partial B}\right)_{T,p} = \frac{\Delta M}{RT} = \frac{N_A \mu \cos \vartheta}{RT} = \frac{\mu \cos \vartheta}{k_B T} \tag{32}$$

(N_A = Avogadro's constant) since the molar change of the magnetic dipole moment due to the reaction (A) equals $N_A \mu \cos \vartheta$ (only the components in the direction of the magnetic field have to be taken into account). Upon putting

$$\varphi_S B = F_S(t) \cos \vartheta \quad \varphi_{T_0} B = F_{T_0}(t) \cos \vartheta \tag{33}$$

(with F_S and F_{T_0} being independent of ϑ), we can transform partial differential equations (23) and (24) to a system of two ordinary linear differential equations for F_S and F_{T_0}, which in matrix notation look

$$\begin{bmatrix} \dot{F}_S + \dfrac{k_{12}k_{21}^{\circ}}{k_{12}^{\circ}} \Theta(T_0)^{\circ} B \\[4mm] \dot{F}_{T_0} - \dfrac{k_{12}k_{21}^{\circ}}{k_{12}^{\circ}} \Theta(T_0)^{\circ} B \end{bmatrix} = \begin{bmatrix} -(k_{12} + 2D_r) & k_{21} \\[4mm] k_{12} & -(k_{21} + 2D_r) \end{bmatrix} \begin{bmatrix} F_S \\[4mm] F_{T_0} \end{bmatrix} \tag{34}$$

There are two cases of degeneracy. One of them concerns $D_r = 0$, i.e. no rotational diffusion. It is described by only one relaxation time, namely the phase (or transverse) relaxation time, t_s, characterizing the decay rate of spin polarization component normal to B. t_s is obtained according to the relation

$$\frac{1}{t_s} = k_{12} + k_{21} \tag{35}$$

On the other hand, if there is no decay rate of radical pair spin polarization (i.e. S—T_0 transitions) but a finite D_r ($k_{12} = k_{21} = 0$), a relaxation time due to Brownian rotational diffusion of radical pair in solution

$$t_r = \frac{1}{2D_r} \tag{36}$$

is found. An adjustment of the relaxation rates can often be achieved by temperature variation. This can be understood in terms of the Debye—Einstein equation, which provides a connection between the effective molecular volume (V_{eff} results from the average radius of a radical pair considered as a sphere), the viscosity η of the solvent, and the temperature

$$\tau_r = V_{eff} \frac{\eta}{k_B T}$$

Both the relaxation times t_s and t_r depend differently upon the rotational

correlation time τ_r (a measure of the Brownian rotational diffusion of radical pairs in solution).

In any event, however, the degeneracy will be destroyed if both the spin polarization as well as the rotational effect must be taken into account. Our main purpose is now to see the conditions under which the system (34) can exhibit stabilities in the steady-state solutions. The condition for having nontrivial solutions of this system is

$$\det |a_{ST_0} - \lambda \delta_{ST_0}| = 0 \tag{37}$$

This equation is known as the characteristic equation. In this case the characteristic equation of (34) yields, in principle, two different eigenvalues: $\lambda_1 = -(k_{12} + k_{21} + 2D_r)$, $\lambda_2 = -2D_r$. Since both Re $\lambda_i < 0$ $(i = 1, 2)$, the steady state $(\Theta(S)^\circ, \Theta(T_0)^\circ)$ is asymptotically stable. Their negative reciprocals represent two relaxation times t_1 and t_2. As is readily determined, we have $t_2 \equiv t_r = -1/\lambda_2$, while for t_s the relation

$$\frac{1}{t_1} \equiv -\lambda_1 = \frac{1}{t_r} + \frac{1}{t_s} \tag{38}$$

holds true. The final solution in terms of $\Theta(S)$ and $\Theta(T_0)$ functions is obtained by means of standard procedures.

Conclusion

The S—T_0 mixing rate discussed in the first part and the relaxation times (t_1, t_s, t_r) discussed in the second part are obviously mutually dependent, and in principle, can be estimated from an analysis of polarization decay curve [23]. In practice the experiment performed largely determined the polarization behaviour. However, we remember that S—T_0 mixing is a slow process and the radical pair must separate before it becomes singlet and is consumed by reaction. Experimental data show t_1 typically 10^{-7}—10^{-4} s. However, sometimes, radical pair partners have sufficiently short relaxation times. Such cases are typical of paramagnetic complex ion and triplet molecules. On the other hand, the fast, chaotic radical pair rotation is dominated by rotation of the partners (R_1, R_2) about their long axes, which may be described by a rotational diffusion constant having value $D_r \approx 10^{10}$ rad s^{-1}. Long reaction times are unusual for radical pairs, however, they have been realized by *Turro* and coworkers [24] and by *Steiner* [25] for reactions occurring in micellar systems.

Apparently, the spin decay and chaotic rotational relaxation behaviour of radical pair depends very much on the order of magnitude by which t_r and $t_1(\leq t_r)$ differ from each other. We further consider the three possible cases.

(i) $t_r \ll t_s$, *i.e.* chaotic rotational diffusion proceeds much faster than the decay rate of spin polarization. Upon this condition eqn (*38*) yields practically $t_l = t_r$.

(ii) $t_r \approx t_s$, *i.e.* rotational diffusion and decay rate spin polarization proceed with comparable rates. Under these circumstances t_r and t_l are different.

(iii) $t_r \gg t_s$, *i.e.* rotational diffusion proceeds much more slowly than the decay rate of spin polarization. Now, application of eqn (*38*) results in $t_l \approx t_s \ll t_r$.

References

1. Atkins, P. V. and Lambert, T. P., *Annu. Rep. Prog. Chem., A 72*, 67 (1975).
2. Matsuzaki, A. and Nagakura, S., *Helv. Chim. Acta 61*, 675 (1978).
3. Valko, L., *The IXth Conference of Czechoslovak Physicists*, Vol. *1*, p. 207. Pardubice, 6—10 July, 1987.
4. Sagdeev, R. Z., Molin, Yu. N., Salikhov, K. K., Leshina, T. V., Kamha, M. A., and Shein, S. M., *Org. Magn. Reson. 5*, 603 (1973).
5. Podoplelov, A. V., Sagdeev, R. Z., Leshina, T. V., Grishin, Yu. A., and Molin, Yu. N., *Dokl. Akad. Nauk SSSR 225*, 866 (1975).
6. Sakuragi, H., Sakuragi, M., Mishima, T., Watanabe, S., Hasegawa, M., and Tokumaru, K., *Chem. Lett. 1975*, 231.
7. Hayashi, H. and Nagakura, S., *Bull. Chem. Soc. Jpn. 51*, 2862 (1978).
8. Turro, N. J. and Kraeutler, B., *J. Am. Chem. Soc. 100*, 7432 (1978).
9. Sakaguchi, Y., Hayashi, H., and Nagakura, S., *Bull. Chem. Soc. Jpn. 53*, 39 (1980).
10. Nagakura, S. and Hayashi, H., *Int. J. Quantum Chem. 18*, 571 (1984).
11. Fowler, W. B., Marrone, M. J., and Kabler, M. N., *Phys. Rev., B 3*, 5909 (1973).
12. Matsuzaki, A. and Nagakura, S., *Bull. Chem. Soc. Jpn. 40*, 359 (1976).
13. Leung, M. and El-Sayed, M. A., *J. Am. Chem. Soc. 97*, 669 (1975).
14. Valko, L., to be published.
15. Adrian, F. J., in *Chemically Induced Magnetic Polarization — Theory, Technique, and Applications.* (Muus, L. T., Atkins, P. W., McLauchlan, K. A., and Pedersen, J. B., Editors.) P. 77. D. Reidel Publishing Company, Dordrecht, 1977.
16. Adrian, F. J., *J. Chem. Phys. 57*, 5107 (1972).
17. Adrian, F. J. and Monchick, L., *J. Chem. Phys. 71*, 2600 (1979).
18. McLauchlan, K. A., Sealy, R. C., and Wittmann, J. M., *Mol. Phys. 36*, 1397 (1978).
19. Nyberg, G., *Mol. Phys. 12*, 69 (1967).
20. Ocelli, R., Quentrec, B., and Brot, C., *Mol. Phys. 36*, 257 (1978).
21. de Kanter, J. J., den Hollander, J. A., Huizer, A. H., and Kaptein, R., *Mol. Phys. 34*, 857 (1977).
22. Valko, L. and Kellö, V., to be published.
23. Hore, P. J., Joslin, C. G., and McLauchlan, K. A., *Chem. Soc. Rev. 8*, 29 (1979).
24. Turro, N. J. and Weed, G. C., *J. Am. Chem. Soc. 105*, 1861 (1983).
25. Ulrich, T. and Steiner, U. E., *Chem. Phys. Lett. 112*, 365 (1984).

Translated by L. Valko