Magnetic Field Effects on Isomerization Reaction

L. VALKO

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

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Dedicated to Professor Ľ. Treindl, in honour of his 60th birthday

We have used the diffusion and rotational Debye–Smoluchowski diffusion-reaction equation to evaluate the chemical kinetics of the intramolecular isomerization reaction of the uncharged radical pairs, influenced by magnetic field effects. A description of isomerization reaction of the uncharged radical pairs demands recognition of both their mutual rotational diffusion and drift under the influence of an external magnetic field. The results indicate that the incorporation of the magnetic field torque effect is manifested in the derived kinetic equations owing to which it influences the isomerization reaction rate. Three possible cases concerning the mutual relative magnitude of the chemical and rotational relaxation processes are discussed.

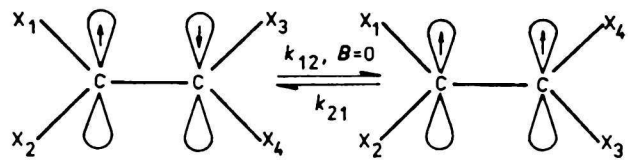
Although magnetic field effects on chemical reaction rates have only recently attracted the attention of the chemists, after all nowadays there is enough experience about the experimental evidence of magnetic field effects on the kinetics of chemical reactions [1]. The so-called radical pair mechanism lying in the heart of these phenomena turned out to be the most valuable key for systematical tracing out magnetic field effects on chemical kinetics. The possible implications of magnetic field effects on chemical reactions depend on the various experimental conditions. For example, as a rule, the unpaired electron spin density in radicals is anisotropic and the reaction occurs thus only at favourable mutual orientations of the reactants – radical partners, in intramolecular radical pair, when the overlap of unpaired electron orbitals is sufficiently great. In this case, mutual rotation of radical fragments in intramolecular pair is of fundamental importance [2], since orientational motion averages radical anisotropic properties. *Salikhov* [3] was the first who considered mutual orientations of the intermolecular radical partners during their recombination reaction.

In paper [2] we have studied the temperature effect on the $S \rightarrow T_0$ transitions in the uncharged radical pairs (permittivity $\varepsilon \rightarrow \infty$) and evaluated the different types of relaxation mechanisms determining the $S \rightarrow T_0$ transitions. However, in that paper we have not taken into account the magnetic field torque effect in solving the rotational Debye–Smoluchowski diffusion-reaction equation.

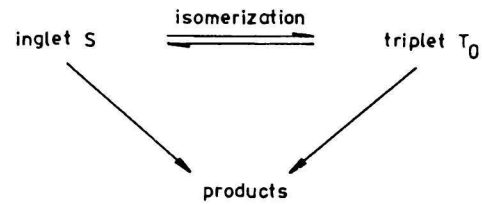
In the light of the recent time-resolved observation of photoisomerization kinetics of substituted ethylenes in the presence of strong external magnetic fields [4—6], we want to introduce in this paper, besides some factors already considered in [2], the above-mentioned magnetic field torque effect influencing intramolecular $S \rightarrow T_0$ transitions, too. Our approach differs substantially from the Salikhov model. It is based on the solution of the Debye–Smoluchowski equation, describing classical precession picture of the spins of the radicals, under a magnetic field torque effect tending to align the resulting radical pair spin momentum parallel to a given axis, identified with the direction of the magnetic field.

THEORETICAL

The unpaired electrons in radicals undergo a spin motion induced by the hyperfine interaction with the nuclear spins. In connection with spin-dependent reaction processes, this motion gives rise to the well known chemically induced dynamic polarization [1]. Recombination of the radical pairs described by the unimolecular isomerization reaction, can be demonstrated by the following kinetic scheme (*A*) where k_{12} and k_{21}, respectively, are the corresponding rate constants. If radical pairs are generated for example by photoisomerization electron transfer in a pure triplet state, the initial spin alignment of the two unpaired electron spins is changed by the hyperfine interaction, and after a few nanoseconds the radical pair assumes a singlet character. External magnetic field, however, can alter the spin motion and give rise to a magnetic field modulation of



(A)



the triplet products. Thus, magnetic field effect is a source of an experimental method for exploring the nanosecond internal dynamics of rotational biradical system. In our previous paper we have introduced [2] the density distribution functions $\Theta_S(\vartheta, t)$ and $\Theta_{T_0}(\vartheta, t)$ in the meaning of radical pair concentrations per solid angle which may change owing to the different precessing rates of the resulting spin vectors $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ in radical pair. The resulting spin vector alternates between S and T_0 orientations, determining thus the mixing of S and T_0 states, which couple the mutual internal rotational diffusion of individual radicals in radical pair.

The concentration of these radical pairs the resulting spin vectors of which have axes pointing at the time t to the solid angle element $d\Omega = 2\pi \sin\vartheta \, d\vartheta$ (ϑ being the angle between the field vector $\boldsymbol{B}$ and a radical pair spin-rotation axis) can be expressed as

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

Isomerization reactions occurring in a magnetic field may be described by the two partial differential equations.

The first of them is the rotational diffusion-reaction equation describing concentration of singlet S state of radical pairs

$$\frac{\partial \Theta(S)}{\partial t} = -v_{12} + D_r \nabla^2 \Theta(S) \qquad (1)$$

where D_r is the concentration-independent mutual rotational diffusion constant of the two individual radicals constituting an intramolecular radical pair.

The second is the rotational Debye–Smoluchowski diffusion-reaction equation [7] which, however, hitherto was not applied to the transport processes occurring in a magnetic field. This equation serves to calculate the rate of the density distribution function of $\Theta(T_0)$ including magnetic field torque effect and could be written as

$$\frac{\partial \Theta(T_0)}{\partial t} = v_{12} + D_r \nabla \left\{ \nabla \Theta(T_0) + \frac{\Theta(T_0)}{k_B T} \left[\boldsymbol{r}_1 \times \nabla_1 V(\boldsymbol{r}_1) + \boldsymbol{r}_2 \times \nabla_2 V(\boldsymbol{r}_2) \right] \right\} = v_{12} + \nabla \{ D_r \nabla \Theta(T_0) + \boldsymbol{J}_B \} \qquad (2)$$

where $\boldsymbol{J}_B$ is the angular diffusive flux of spin-axes directed by the field $\boldsymbol{B}$, k_B is the Boltzmann constant, T the absolute temperature, and $V(\boldsymbol{r}_i)$ is the potential energy interaction of an i-th unpaired electron ($i = 1, 2$) with a magnetic field at the position $\boldsymbol{r}_i$ relative to the nucleus of an atom bearing an unpaired electron. The reaction rate v_{12} is represented by

$$v_{12} = -\left(\frac{\partial \Theta(S)}{\partial t} \right)_{spin} = \left(\frac{\partial \Theta(T_0)}{\partial t} \right)_{spin} = k_{12}\Theta(S) - k_{21}\Theta(T_0) = k_{21}[K\Theta(S) - \Theta(T_0)] \qquad (3)$$

It should be emphasized that owing to the perturbation of the $S \rightarrow T_0$ transition influenced by the magnetic field the rate constants k_{12} and k_{21} as well as the corresponding equilibrium constant $K \equiv k_{12}/k_{21}$ depend on the field $\boldsymbol{B}$ and angle ϑ. In the absence of field, *e.g.* $\boldsymbol{B} = 0$, they are, of course, identical with k_{12}°, k_{21}°, and $K^{\circ} \equiv k_{12}^{\circ}/k_{21}^{\circ}$.

To complete our description of electronic spin motion in the magnetic field we must evaluate the expression for the angular diffusive flux $\boldsymbol{J}_B$ of resulting spin vectors $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ directed by the magnetic field $\boldsymbol{B}$

$$\boldsymbol{J}_B = D_r \frac{\Theta(T_0)}{k_B T} \left[\boldsymbol{r}_1 \times \nabla_1 V(\boldsymbol{r}_1) + \boldsymbol{r}_2 \times \nabla_2 V(\boldsymbol{r}_2) \right] \qquad (4)$$

Magnetic field $\boldsymbol{B}$ produces an interaction potential energy $V(\boldsymbol{r}_1, \boldsymbol{r}_2)$ which may be for a radical pair specified as

$$V(\boldsymbol{r}_1, \boldsymbol{r}_2) = V(\boldsymbol{r}_1) + V(\boldsymbol{r}_2) = e(\boldsymbol{v}_1 \boldsymbol{A}(\boldsymbol{r}_1) + \boldsymbol{v}_2 \boldsymbol{A}(\boldsymbol{r}_2)) \qquad (5)$$

Here $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$ are the velocities of radical pair electrons, $\boldsymbol{A}(\boldsymbol{r}_1)$ and $\boldsymbol{A}(\boldsymbol{r}_2)$ are the magnetic vector potentials of the field $\boldsymbol{B}$ at the distance $\boldsymbol{r}_i$ (i = 1, 2) from the nucleus of a considered atom and $-e$ is the charge of the electron. Let us consider now the following vector relation

$$\nabla(\boldsymbol{v}\,.\,\boldsymbol{A}(\boldsymbol{r})) = \mathrm{grad}\,(\boldsymbol{v}\,.\,\boldsymbol{A}(\boldsymbol{r})) = (\boldsymbol{v}\nabla)\boldsymbol{A}(\boldsymbol{r}) + (\boldsymbol{A}(\boldsymbol{r})\nabla)\boldsymbol{v} + \\ + \boldsymbol{v} \times \mathrm{rot}\,\boldsymbol{A}(\boldsymbol{r}) + \boldsymbol{A}(\boldsymbol{r}) \times \mathrm{rot}\,\boldsymbol{v} \qquad (6)$$

Let us now consider an electron of charge $-e$ in an external magnetic field $\boldsymbol{B}(\boldsymbol{r}, t)$ generated by the vector potential $\boldsymbol{A}(\boldsymbol{r}, t)$ which defines $\boldsymbol{B}(\boldsymbol{r}, t)$ through

$$\boldsymbol{B}(\boldsymbol{r}, t) = \nabla \times \boldsymbol{A}(\boldsymbol{r}, t)$$

The equation of motion of the electron $m_e\boldsymbol{v} = \boldsymbol{F}_L$ when the Lorentz force $\boldsymbol{F}_L$ depends upon the field but not on the vector potential

$$\frac{\mathrm{d}}{\mathrm{d}t}(m_e\boldsymbol{v} - e\boldsymbol{A}) = -e(\boldsymbol{v}\nabla)\boldsymbol{A} - e(\boldsymbol{v} \times \mathrm{rot}\,\boldsymbol{A})$$

can be derived from the classical Lagrangian

$$\mathcal{L}(\boldsymbol{r}, \dot{\boldsymbol{r}}, t) = \frac{1}{2}mv^2 - e\boldsymbol{v}\,.\,\boldsymbol{A}$$

Now, taking into consideration the substantial derivative $\mathrm{d}\boldsymbol{A}/\mathrm{d}t$

$$\frac{\mathrm{d}\boldsymbol{A}}{\mathrm{d}t} = \frac{\partial \boldsymbol{A}}{\partial t} + (\boldsymbol{v}\nabla)\boldsymbol{A}$$

then

$$\boldsymbol{F}_L = m_e\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} = -e\frac{\partial \boldsymbol{A}}{\partial t} - e(\boldsymbol{v} \times \mathrm{rot}\,\boldsymbol{A})$$

Considering a time-independent magnetic field, *e.g.* $\partial\boldsymbol{A}/\partial t = 0$, then

$$\boldsymbol{F}_L = -e(\boldsymbol{v} \times \boldsymbol{B})$$

and

$$\nabla V = \nabla(e\boldsymbol{v}\,.\,\boldsymbol{A}) = e(\boldsymbol{v} \times \boldsymbol{B}) \qquad (7)$$

Here, we accept an idea that the influence of the external magnetic field is solely represented by the quantum version of the Lorentz force term $\boldsymbol{F}_L$.

$$\boldsymbol{J}_B = D_r\frac{e\,\Theta(T_0)}{k_BT}\left[\boldsymbol{r}_1 \times \boldsymbol{v}_1 \times \mathrm{rot}\,\boldsymbol{A}(\boldsymbol{r}_1) + \right. \\ \left. + \boldsymbol{r}_2 \times \boldsymbol{v}_2 \times \mathrm{rot}\,\boldsymbol{A}(\boldsymbol{r}_2)\right] \qquad (8)$$

As the magnetic vector potential giving rise to an external magnetic field $\boldsymbol{B}$ is

$$\mathrm{rot}\,\boldsymbol{A}(\boldsymbol{r}_i) = \boldsymbol{B} \qquad (i = 1, 2)$$

then for $\boldsymbol{J}_B$ we may write

$$\boldsymbol{J}_B = D_r\frac{e\,\Theta(T_0)}{m_ek_BT}(\boldsymbol{S}_1 + \boldsymbol{S}_2) \times \boldsymbol{B}$$

or

$$\boldsymbol{J}_B = -D_r\frac{\Theta(T_0)}{k_BT}(\boldsymbol{\mu}_1 + \boldsymbol{\mu}_2) \times \boldsymbol{B} = \\ = -D_r\frac{\Theta(T_0)}{k_BT}(\boldsymbol{\mu} \times \boldsymbol{B}) \qquad (9)$$

where m_e is the mass of the electron, $\boldsymbol{\mu}_1$, $\boldsymbol{\mu}_2$ are the magnetic dipoles which are related with the spin vectors $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ by the equations

$$\boldsymbol{\mu}_1 = -\gamma\boldsymbol{S}_1 \quad \boldsymbol{\mu}_2 = -\gamma\boldsymbol{S}_2$$

where $\gamma = e/m_e$ is the so-called gyromagnetic ratio of the electron and e and m_e are its charge and mass, respectively. Naturally, $\boldsymbol{\mu} = \boldsymbol{\mu}_1 + \boldsymbol{\mu}_2$ is the resulting magnetic dipole of a radical pair in the triplet T_0 state.

We can see that $\boldsymbol{\mu} \times \boldsymbol{B}$ is the torque $\boldsymbol{\tau}_B$ affecting the magnetic dipole of a radical pair. Thus the magnetic field produces a couple of strength

$$\boldsymbol{\tau}_B = \boldsymbol{\mu} \times \boldsymbol{B} \qquad (10)$$

or

$$\tau_B = \mu B \sin\vartheta \qquad (10a)$$

tending to twist magnetic moment $\boldsymbol{\mu}$ into line with $\boldsymbol{B}$, and this torque forces the spin vector (magnetic dipole) of radical pair to precess around a cone, making a constant angle ϑ with the field (Fig. 1).

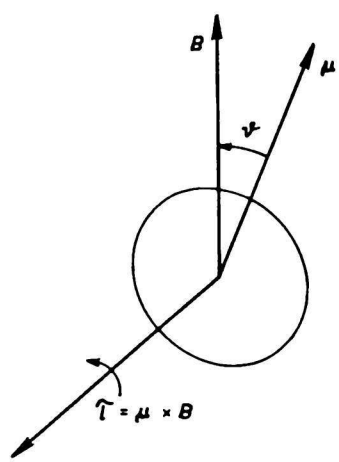


Fig. 1. The torque exerted on a magnetic dipole in a magnetic field $\boldsymbol{B}$.

Solution of the Rotational Debye–Smoluchowski Diffusion Equation

Taking into consideration the results of preceding section we are now in a position to solve the diffusion eqns (*1*) and (*2*).

Application of the Laplace operator Δ enables us to write eqn (*1*) as

$$\frac{\partial\Theta(\mathrm{S})}{\partial t} = -v_{12} + D_r \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left[\sin\vartheta\frac{\partial\Theta(\mathrm{S})}{\partial\vartheta}\right] \quad (11)$$

Substituting eqn (9) for $\boldsymbol{J}_B$ with respect to eqn (10) into eqn (2), the Debye–Smoluchowski equation (9) could be written as

$$\frac{\partial\Theta(\mathrm{T}_0)}{\partial t} = v_{12} + D_r \nabla^2 \Theta(\mathrm{T}_0) + \mathrm{div}\boldsymbol{J}_B \quad (12)$$

Expressing the Laplace $\nabla^2 \equiv \Delta$ and the Hamilton ∇ operator in polar coordinates, eqn (12) could be written as

$$\frac{\partial\Theta(\mathrm{T}_0)}{\partial t} = v_{12} + D_r \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left[\sin\vartheta\frac{\partial\Theta(\mathrm{T}_0)}{\partial\vartheta}\right] - D_r \frac{\mu B}{k_B T}\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left[\sin^2\vartheta\,\Theta(\mathrm{T}_0)\right] \quad (13)$$

Fortunately it will not be necessary to find the general solution of eqns (11) and (13). Since $\mu B/k_B T \ll 1$ (usually by orders of magnitude), the magnetic field causes only very slight deviations from the state corresponding to $\boldsymbol{B} = 0$, *i.e.* random distribution radical pair spin-axes with respect to the direction of an applied magnetic field $\boldsymbol{B}$. Therefore, we expand $\Theta(\mathrm{S})$ and $\Theta(\mathrm{T}_0)$ as a Taylor series in $\mu B/k_B T$, denoting the coefficients of successive powers of $\mu B/k_B T$ by $\varphi_S(\vartheta, t)$ and $\varphi_{T_0}(\vartheta, t)$

$$\Theta(\mathrm{S}) \approx \Theta(\mathrm{S})^\circ + \frac{\mu B}{k_B T}\varphi_S(\vartheta, t) + \quad (14)$$

$$\Theta(\mathrm{T}_0) \approx \Theta(\mathrm{T}_0)^\circ + \frac{\mu B}{k_B T}\varphi_{T_0}(\vartheta, t) + \ldots \quad (15)$$

where

$$\Theta(\mathrm{S})^\circ = \frac{\langle c(\mathrm{S})^\circ\rangle}{4\pi} \qquad \Theta(\mathrm{T}_0)^\circ = \frac{\langle c(\mathrm{T}_0)^\circ\rangle}{4\pi} \quad (16)$$

and

$$K^\circ = \frac{\Theta(\mathrm{T}_0)^\circ}{\Theta(\mathrm{S})^\circ} = \frac{k_{12}^\circ}{k_{21}^\circ}, \quad \text{and} \quad K = \frac{k_{12}}{k_{21}} \quad (\boldsymbol{B} \neq 0) \quad (17)$$

Any term of the second or higher order in the magnetic field ($\mu B/k_B T$) will be neglected. Now, inserting eqns (14) and (15) into the rate term v_{12} (eqn (3)) leads to

$$v_{12} = k_{12}\Theta(\mathrm{S})^\circ - k_{21}\Theta(\mathrm{T}_0)^\circ + \frac{\mu B}{k_B T}\left[k_{12}\varphi_S(\vartheta, t) - k_{21}\varphi_{T_0}(\vartheta, t)\right] + \ldots$$

and after rearrangement of the first term with respect to eqns (17)

$$v_{12} = \frac{k_{12}k_{21}^\circ}{k_{12}^\circ}\Theta(\mathrm{T}_0)^\circ B\left(\frac{\partial(\ln K)}{\partial B}\right)_{T,p} + \frac{\mu B}{k_B T}\left[k_{12}\varphi_S(\vartheta, t) - k_{21}\varphi_{T_0}(\vartheta, t)\right] + \quad (18)$$

where we denoted $K - K^\circ \equiv \delta K$.

Now, if ΔM represents the change of the overall molar magnetic dipole moment M which is produced by reaction (proceeding from the left to the right) while keeping the intensive variables T and p constant, then [8]

$$\left(\frac{\partial(\ln K)}{\partial B}\right)_{T,p} = \frac{\Delta M}{RT} = \frac{N_A \mu\cos\vartheta}{RT} = \frac{\mu\cos\vartheta}{k_B T} \quad (19)$$

(N_A – Avogadro's constant) since the change of the molar magnetic dipole moment due to the reaction scheme (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 (separation condition)

$$\varphi_S(\vartheta, t)B = F_S(t)\cos\vartheta$$
$$\varphi_{T_0}(\vartheta, t)B = F_{T_0}(t)\cos\vartheta \quad (20)$$

(with F_S and F_{T_0} being independent on ϑ), we can transform partial differential equations (11) and (13) to a system of two ordinary linear differential equations for F_S and F_{T_0}, which in matrix notation look as

$$\begin{bmatrix} \dot{F}_S + k_{21}\Theta(\mathrm{T}_0)^\circ B \\ \dot{F}_{T_0} - (k_{21} - 2D_r)\Theta(\mathrm{T}_0)^\circ B \end{bmatrix} = \begin{bmatrix} -(k_{12} + 2D_r) & k_{21} \\ k_{12} & -(k_{21} + 2D_r) \end{bmatrix}\begin{bmatrix} F_S \\ F_{T_0} \end{bmatrix} \quad (21)$$

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 chemical relaxation time t_{ch}, characterizing the $\mathrm{S} \rightarrow \mathrm{T}_0$ transitions. t_{ch} is obtained according to the relation

$$\frac{1}{t_{ch}} = k_{12} + k_{21} \quad (22)$$

On the other hand, if there is no chemical relaxation (*i.e.* $\mathrm{S} \rightarrow \mathrm{T}_0$ transitions) but a finite D_r ($k_{12} = k_{21} = 0$), a relaxation time due to Brownian rotational diffusion of resulting magnetic moment of radical pair in solution

$$t_r = \frac{1}{2D_r} \quad (23)$$

is found. An adjustment of the relaxation rates can often be achieved by temperature variation [2].

However, the degeneracy will be destroyed if both the electron spin polarizations as well as the rotational effect must be taken into account. Our main purpose is now to see the conditions under which the system (*21*) can exhibit stabilities in the steady-state solutions. The condition for having nontrivial solutions of this system is

$$\det \left| a_{ST_0} - \lambda \delta_{ST_0} \right| = 0 \qquad (24)$$

where the Kronecker delta is defined by $\delta_{ST_0} = 1$ if $S = T_0$; $\delta_{ST_0} = 0$ if $S \neq T_0$. This equation is known as the characteristic equation. In this case the characteristic equation (*21*) 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 $t_2 \equiv t_r = -1/\lambda_2$, or

$$t_r = \frac{1}{2D_r} \qquad (25)$$

while for t_1 the relation

$$\frac{1}{t_1} = -\lambda_1 = \frac{1}{t_r} + \frac{1}{t_{ch}} \qquad (26)$$

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

DISCUSSION

Here we describe an isomerization occurring through uncharged radical pairs formation in the framework of classical spin dynamics [9]. In more technical terms, the quantum mechanical spin motion of radical pair electrons is claimed to be equivalent to a classical rotational Brownian diffusion process [6]. In this paper the problem of isomerization reaction of isolated uncharged radical pair in solution has been modelled using the rotational Debye–Smoluchowski diffusion-reaction equation in which we have incorporated magnetic field torque effect. Since an external magnetic field is present in the system, the problem is relatively complex, therefore we confined ourselves for the solution linear in $\mu B/k_B T$ Under such a condition the partial differential diffusion-reaction equations are reduced to a system of the two ordinary and linear kinetic differential equations for the two time-dependent distributions.

Distribution functions at a given time manifest the isomerization reaction yields, since $F_S(t) + F_{T_0}(t) = 1$. The possibility of simultaneous recombination *via* singlet (S) and triplet (T_0) states is typical for radical-ion pair reactions. In the majority of the cases, the ground state of recombination products is singlet. However, the minor triplet T_0 recombination channel cannot be eliminated [10]. In our simple presented model we accept this model of uncharged radical pair recombination mechanism represented by the scheme *A*, too. On the other hand, the intersystem crossing between T_0 and triplet T_+ and T_- states induced by the hyperfine interaction is appreciably diminished in the presence of strong magnetic fields thereby attenuating the quantum yield of the triplet radical pair [4].

It is quite obvious that any factors decreasing the uncharged radical pairs lifetime should hinder the minor recombination channel manifestation. These could be, *e.g.* the molecule–ion charge transfer reactions, relaxation and the reaction of the radicals with the solvent molecules. Otherwise, cage-radical pair lifetimes depend on many factors – radical reactivity, mutual radical rotational diffusion and different type of interactions between radical pairs. Characteristic radical pair lifetimes are as a rule in the range of $t_1 = 10^{-10}$ to 10^{8} s when rotational diffusion constant is $D_r \approx 10^{10}$ rad s^{-1}

The orientational relaxation kinetics is characterized by favourable mutual orientations of radical partners. In the case of geminate isomerization, the radical orientation of the primary pair favours the reaction while a radical rotation reduces the reaction probability [9].

Apparently, the chemical and rotational relaxation behaviour of a 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) $t_r \ll t_{ch}$, *i.e.* recombination of radical pairs undergoing free Brownian motion proceeds much faster than the chemical relaxation. Upon this condition eqn (*26*) yields practically $t_1 = t_r$.

ii) $t_r \approx t_{ch}$, *i.e.* rotational diffusion and chemical relaxation proceed with comparable rates. Under these circumstances t_r and t_1 are different.

iii) $t_r \gg t_{ch}$, *i.e.* rotational diffusion proceeds much more slowly than the chemical relaxation. Now, application of eqn (*26*) results in $t_1 \approx t_{ch} \ll t_r$.

For the model discussed, these relaxation times are determined first of all by the solvent viscosity, solvent dielectrical permittivity and the diffusion constant.

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Solvolysis of Thioamides in Alkaline Region in the System of Water–Ethanol

†J. MOLLIN and E. KARÁSKOVÁ

Department of Inorganic and Physical Chemistry, Faculty of Natural Sciences, Palacký University, CS-771 46 Olomouc

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The rate constants of alkaline solvolysis of *N,N*-diphenylthiobenzamide and 4-chloro-*N,N*-dimethylthiobenzamide have been measured. The change in the reaction order with respect to the base concentration, conditioned by change in composition of the solvent, has been discussed on the basis of Taft's mechanisms and equilibrium between the hydroxide and ethoxide ions.

Alkaline solvolysis of thioamides was studied many times [1—6] and the literature agrees in that the reacting component is the neutral thioamide molecule. In aqueous medium the reaction is of first order with respect to concentration of OH ions [1—4, 6], while in the mixture of water—ethanol the reaction order with respect to the total base concentration was found, in some cases, to be higher [5, 6] and changing also with the change of the solvent [6]. Therefore, it seemed to be of interest to gather further data in experiments using solvents with higher content of ethanol and tertiary thioamides as reacting substrates, so that the result was not loaded with error due to possible dissociation of the electrophile.

EXPERIMENTAL

N,N-Diphenylthiobenzamide [7] and 4-chloro-*N,N*-dimethylthiobenzamide [8] were prepared according to the respective literature. The purity of the compounds was checked by determination of melting points and by elemental analysis. The 5×10^{-4} M solutions of the presented compounds were prepared in the mixture of water–ethanol (*N,N*-diphenylthiobenzamide in mixtures of 30, 70, and 90 mass % of ethanol in water and 4-chloro-*N,N*-dimethylthiobenzamide in mixtures of 70 and 90 mass % of ethanol in water). The pH of the solution was adjusted by NaOH solution in the same solvent. For preparation of solutions distilled water, ethanol for UV measurement and NaOH of anal. grade (both from Lachema, Brno) were used. The pH of the reaction mixture could not be measured directly due to substrates interfering in setting of a reproducible potential of the hydrogen electrode.

Therefore, the solutions were prepared without the substrate in the same solvent of the same concentration of NaOH as in the respective reaction mixture. The pH of these solutions were measured by using hydrogen and silver chloride electrodes, while the function of the electrode system was checked by series of buffers [9—11].

The reacting system was analyzed by an E-7 polarograph (Laboratorní přístroje, Prague) with mercury drop electrode (drop time = 2.6 s).