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Spin effects in intramolecular electron transfer in naproxen-N-methyl-pyrrolidine dyad.

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Abstract

The intramolecular electron transfer in the naproxen-N-methyl-pyrrolidine dyad has been investigated by spin chemistry methods. The existence of CIDNP in a high magnetic field points to electron transfer as a possible mechanism of the quenching of the excited state of a dyad. However, the failure to detect magnetic field effects on triplet yield makes us conclude that this quenching mechanism is not the only one. The observation of CIDNP effects in the dyad in the media of low polarity and the short risetime of triplet state formation indicate a potential role of exciplex in the quenching of the excited state of the dyad.

Introduction

The nature of chirality effects on chemical processes has been a matter of current interest for many years. This interest is inspired by the importance of optical isomers for the different scientific areas, i.e., from the problems connected with the origin of life on the Earth, to the pharmacological problems of the varying remedial activity of drug enantiomers [1, 2, 3]. Understanding the chirality effect on chemical reactivity is the challenge in modern chemistry.

At present, there are only a few examples of the influence of chirality on photochemical processes [4, 5, 6, 7, 8, 9, 10, 11, 12]. The difference in the radical transformation of the (R) and (S) enantiomers of 2-phenylpropionic acid in the reaction with 4-methyl-2-quinolinecarbonitrile was detected using spin chemistry methods [13]. Later attempts to verify the magnetic field effect (MFE) on this reaction were unsuccessful [14, 15, 16, 17]. The difference in the

configuration-dependent fluorescence quenching in the *R,S* and *S,S* naproxen - pyrrolidine dyads ((*S*)-*N*-methyl-2-pyrrolidinemethyl 2 (*R*) or (*S*)-(6-methoxy-2-naphthylpropanoate) (Chart 1) have been recorded quite recently [18, 19].

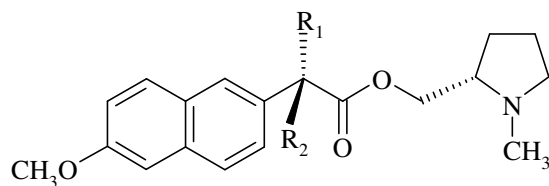


Chart 1. Structures of naproxen-pyrrolidine dyads.

The intramolecular electron transfer between the naproxen (NPX) and the *N*-methylpyrrolidine (PYR) fragments was assumed to be the major mechanism of NPX excited state deactivation. The electron transfer rate constants of (*S,S*)- and (*R,S*)-(NPX–PYR) were calculated from the ratio between the fluorescence quantum yield and the lifetime measured in acetonitrile and found to be $1.8 \times 10^8 \text{ s}^{-1}$ and $2.8 \times 10^8 \text{ s}^{-1}$ for the (*S,S*) and (*R,S*) isomers, respectively. The main goal of this report is to gain further insight into the photophysical processes occurring in NPX–PYR dyads by means of spin chemistry methods.

Experimental

The *R,S* and *S,S* naproxen - pyrrolidine ester dyads ((*S*)-*N*-methyl-2-pyrrolidinemethyl 2 (*R*) or (*S*)-(6-methoxy-2-naphthylpropanoate) were synthesized as described elsewhere [19]. 2-Methyl-naphthalene (Aldrich) was sublimated prior to using. Triethylamine (TEA) was distilled under zinc powder. Deuteroacetonitrile (D99.9%) and deuterobenzene (D99.8%) (both from Aldrich) were used in NMR and CIDNP experiments. Acetonitrile, freshly distilled over P_2O_5 , and tetrahydrofuran, purified using standard technique described in [20] just before experiments on magnetic field effect.

The 1D ^1H NMR spectra were recorded at room temperature on a DPX200 BRUKER NMR spectrometer (200 MHz ^1H operating frequency, $\tau(90^\circ) = 5.8 \mu\text{s}$). All samples were bubbled with argon for 15 min to remove dissolved oxygen just before photolysis. The samples in standard 5 mm Pyrex NMR tubes were irradiated directly in the probe of an NMR spectrometer. The Lambda Physik EMG 101 MSC eximer laser was used as a light source (308 nm, 100 mJ at output window, 20 mJ/pulse in sample volume, with a pulse duration of 15 ns). For the time resolved (TR) CIDNP experiments [21, 22], the delay time between the laser and

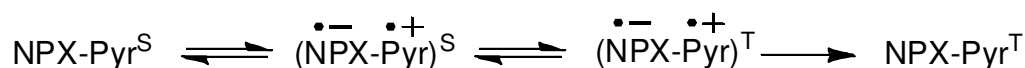
detecting pulses varied from 0 to 100 μ s. The pseudo steady-state (PSS) photo-CIDNP [23] and TR CIDNP experiments were performed for a mixture, containing 1mM of either (*S,S*)- or (*R,S*)- (NPX–PYR) with or without 3 mM of TEA. Solvent polarity was varied by changing the proportion of the deuterobenzene/deuteroacetonitrile mixture. All samples were bubbled with argon for 15 min to remove dissolved oxygen just before photolysis.

The influence of external magnetic field on the triplet of (NPX–PYR) dyads formation were investigated by using laser flash photolysis technique ($\lambda_{exit} = 266$ nm, pulse length 10 ns, energy 12 mJ) and electromagnet. This apparatus was described earlier [24]. Concentration of the dyad was 0.2 mM in acetonitrile and tetrahydrofuran.

Results and Discussion

A large body of research on the molecular dynamics of dyads, triads and chain-linked systems (molecules where donor and acceptor groups are divided by different spacers), performed by means of magnetic field effects analysis (see for example [25, 26]), encouraged us to look for the MFE in the formation of the triplet state of the NPX-PYR dyad.

Scheme 1. Intramolecular electron transfer in NPX-PYR dyad.



Since triplet formation includes a stage of singlet–triplet conversion in biradical ions (Scheme 1), in terms of spin chemistry principles, the yield of the dyad’s triplet state is expected to depend on the external magnetic field strength. In the case of the weak electron exchange interaction (*J*), comparing to hyperfine interaction (HFI) constants between the donor and acceptor fragments of the dyad biradical ion, the usual HFI- and Δ *g*-mechanisms must be involved in spin evolution [27]. For the strong electron exchange interaction, additional mechanisms are feasible, i.e., the electron relaxation induced spin state transitions and the level-crossing (*J*) mechanism [28]. In the latter, the dependence of triplet yield on external magnetic field can be correlated with the value of average electron exchange coupling in a radical ion pair (RIP), $H_{\text{max}} \sim 2J_0$. The $2J_0$ value of the majority of the investigated biradicals with a chain length of 6-10 carbon atoms, which is close to that in the NPX–PYR dyad, amounts to about 10-50 mT [25, 29, 30, 31]. In this study the MFE was measured in the magnetic field range of up to 70 mT. In this case, we expected that a maximum of the triplet yield dependence on external magnetic field will lie in the low MF range because of a more rigid structure. The HFI constants and the difference in the *g*–factors of donor and acceptor fragments in the biradical ion allowed us to

assume the appearance of MFE via the HFI and relaxation mechanisms in the MF range chosen [27].

The foregoing is verified by measuring the MFE on the yield of the dyad's triplet state ($\lambda_{\text{obs}} = 440 \text{ nm}$ [18, 19]) with the help of laser flash photolysis technique. Figure 1 shows the kinetic curve for the NPX-Pyr triplet.

The triplet yield dependence on MF was measured at the maximum of these curves in acetonitrile and tetrahydrofuran, but no effect could be observed (Figure 2).

The absence of MFE might be due to the wrong choice of the range of magnetic field magnitude. This could be the case if the energy of electron exchange interaction in biradical ions was much higher than the value of the applied external MF. According to our previous calculations [32], in radical pairs with $J > A$ (HFI constant), the absence of the MFE formed through the HFI mechanism is also possible. On the other hand, a very quick growth of the triplet signal (for about 20 ns), identical in both solvents, acetonitrile and tetrahydrofuran, was detected. In addition, we observed almost a three-fold decrease in the intensity of the triplet transient absorption in acetonitrile as compared with that in tetrahydrofuran. These results allow the assumption that the photoinduced electron transfer (PET) stage might not be the only way of triplet state population.

Note that the typical photoinduced processes, expected to occur between the excited naphthalene chromophores and the electron donors like amines, include both PET and exciplex formation [18, 19, 25, 26, 27]. **Thus**, these two pathways should be considered as the main quenching mechanisms. The detection of weak exciplex emission upon fluorescence measurements with dyads in acetonitrile was described in [18]. The feasible hydrogen or energy transfer can be excluded. The calculation performed in terms of the Rehm–Weller equation

$$\Delta G_{\text{exc}} = E_{\text{ox}} - E_{\text{red}} - E_{0-0} + \frac{2.6 \text{ eV}}{\epsilon} - 0.13 \text{ eV}$$

and

$$\Delta G_{\text{exc}} = E_{\text{ox}} - E_{\text{red}} - E_{0-0} - \frac{\mu^2}{\rho^2} \left(\frac{\epsilon - 1}{2\epsilon + 1} - 0.19 \right) + 0.38 \text{ eV}$$

using $E_{\text{ox}}(\text{N-methylpyrrolidine}) = 1.0 \text{ V}$, and $E_{\text{red}}(\text{2-methoxynaphthalene}) = -2.6 \text{ V}$ and $E_{0-0}(\text{NPX}) = 3.69 \text{ eV}$ shows that in the system under study, exciplex formation is favored in non-polar and weak polar solvents, while in polar media, the photoinduced electron transfer between the singlet excited state of naproxen and pyrrolidine fragment must prevail (Figure 3). The possibility of the PET between the excited triplet state of the naproxen and pyrrolidine fragment of dyad was discussed in the [18]. It was shown that this process is thermodynamically

unfavourable. Besides that laser flash photolysis experiments has showed that triplet transient absorptions of NPX –PYR dyad and naproxen decay with virtually the same kinetics [18].

The failure to detect the MFE led us to use another spin chemistry method, i.e., the chemically induced dynamic nuclear polarization (CIDNP) in high fields, to detect the PET stage. Figure 4 shows the NMR and CIDNP spectra for the *S,S* isomer of the dyad in acetonitrile. Note that the *R,S* isomer demonstrates the same CIDNP effects. The noticeable CIDNP effects were detected only for pyrrolidine protons at α -position relative to the N atom. It is assumed then that this polarization is derived from the biradical ion because of HFI constants of amine radical cation are maximal on N-CH₃, N-CH₂ and N-CH groups in the system under study [33]. One can suggest that this polarization is formed through the S–T₀ mechanism in accordance with the results of previous investigations on chemical polarization observed in short-lived biradicals in high MF during the photolysis of cyclic ketones [27], alkaloids lappaconitine [34], and benzoquinone in the presence of quadricyclane [35]. The possibility of the appearance of S–T₀ mechanism in the process of back electron transfer in NPX –PYR dyad might be related to one of the following processes: chemical reaction, fast relaxation in the biradical ion or the nuclear relaxation of back electron transfer product – long-lived triplet state.

An indicative feature of the CIDNP effects, formed in radical ion pairs, is their high sensitivity to solvent polarity [27]. In this study, the dependence of the CIDNP effects of N-methylpyrrolidine protons on the dielectric solvent constant, (ϵ), was measured to gain insight into the reaction mechanism. The acetonitrile/benzene mixtures in different ratios were used as the solvent.

Note that the CIDNP effects observed for the dyad are the overall result of several contributions. These include both the biradical ion recombination from the S and T states (intramolecular back electron transfer), and the bimolecular quenching of the chromophore excited state of the dyad by another dyad in the ground state, as well as the contribution from the processes, occurring in the bulk. The latter results from both the degenerate electron exchange between radical ions with neutral dyad molecules and from the F-pairs. To minimize the contribution from intermolecular processes to CIDNP, we have used the relatively low concentrations of the NPX–PYR dyad around 10⁻³ M and added triethylamine (TEA) as an external quencher of the naproxen excited state. In this case, the rate of intramolecular quenching of the excited singlet state of the dyad significantly exceeds those of intermolecular processes: $w_{\text{intra}} = 1.8 \times 10^8 \text{ s}^{-1}$ and $2.8 \times 10^8 \text{ s}^{-1}$ for the (*S,S*)- and the (*R,S*)-configuration, respectively; $w_{\text{TEA}} = 5 \times 10^9 \times 10^{-2} \text{ s}^{-1}$ and $w_{\text{inter}} = 5 \times 10^9 \times 10^{-3} \text{ s}^{-1}$. It was assumed that the rate constants of the quenching of dyad the excited state both the dyad itself and by amine are of the same values [18, 19, 33].

The experimental dependences of the integral intensity of the TR CIDNP of N-methylpyrrolidine protons (N-CH₃ and N-CH) and TEA N-CH₂ protons on solvent polarity (ϵ) are presented in Figure 5 (a,b). For comparison, Figure 6 shows the dependence of the CIDNP effects of the TEA protons on solvent polarity in a bimolecular reaction with parent naphthalene. The comparison of these Figures indicates that the solvent-dependence of the CIDNP effects on N-methylpyrrolidine differs significantly from that observed for the naphthalene +TEA system. Note that these systems have very close values of redox potentials: methoxynaphthalene, $E_{\text{red}} = 2.60$ V; naphthalene, $E_{\text{red}} = 2.58$ V; triethylamine, $E_{\text{ox}} = 0.96$ V [36]. Moreover, the protons of N-methyl pyrrolidine of the NPX-PYR dyad and the TEA protons, detected in the reactions with dyad (Figure 5), manifest the CIDNP effects in the media with low polarity in contrast with the naphthalene + TEA system (Figure 6).

In addition, the dependence of the signal from TEA CH₂ protons, detected in the photoinduced interaction between TEA and the dyad changes the CIDNP sign (Figure.5).

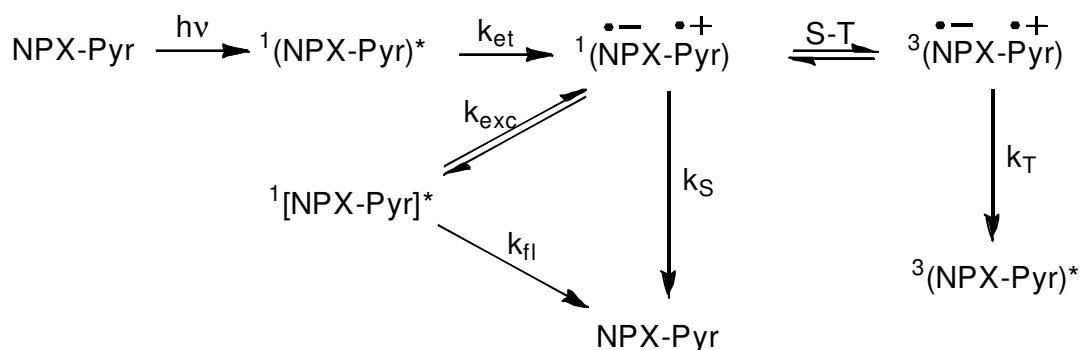
To explain the unusual CIDNP dependences on the solvent polarity, we consider the reference data. According to classical considerations, the S-type curve is the typical shape of the dependence of the quantum yields of solvent separated RIP on solvent polarity [37]. On the other hand, under UV irradiation, the charge transfer complexes of stilbene with fumaronitrile form stilbene radical cations also in low polarity solvents: brombenzene and dimethoxyethane [38]. The authors assume that the presence of radical cations in nonpolar solvents is due to the fast (comparable with RIP lifetime) transitions between the separated and contact RIP. The observation of the MFE in exciplex fluorescence in both the chain-linked phenanthrene – dimethylaniline dyad and the supramolecular complex of zinc(II)-tetraphenylporphyrin with viologen, described by Japanese researchers [39], was also assigned to the fast equilibrium between RIP and exciplex.

For the NPX-PYR dyad, the main piece of evidence for exciplex participation in the quenching of the excited state is the appearance of CIDNP in media with low polarity and the difference between the CIDNP signs of the TEA protons in solvents of high and low polarity.

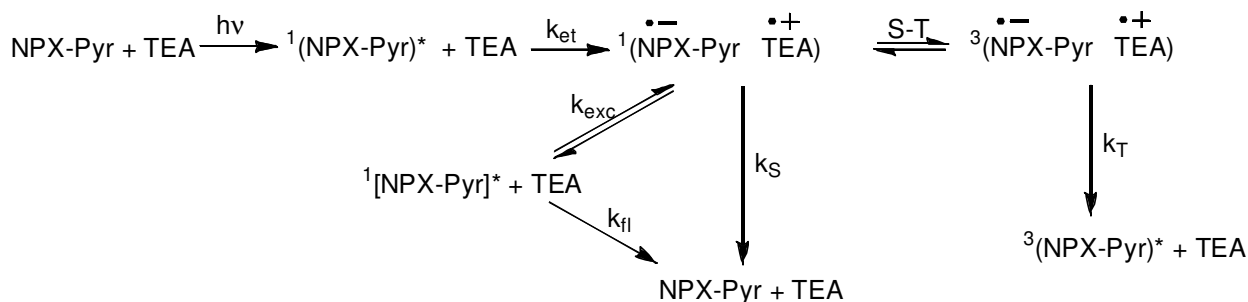
Since the CIDNP intensity is mainly governed by RIP concentration, the difference in the curves of Figures 5 and 6 reflects distinctions between the processes occurring in the separated RIP of radical ions and the linked donor-acceptor fragments of the biradical ion. Thus, the remarkable TEA CIDNP of the “naphthalene + TEA” system arises in the media with a dielectric constant ~ 20 . At the same time, this dependence, measured for the NPX-PYR dyad, with the polarographic half-wave potentials identical to those of the previous system, demonstrates the maximum CIDNP at $\epsilon = 7$. This directly indicates the formation of radical ions in the media of

weak polarity. Schemes 2 and 3 show the processes of excited state decay with the participation of exciplex with and without TEA.

Scheme 2. The decay of the dyad excited state, resulting in CIDNP formation.



Scheme 3. The decay of the dyad excited state in the presence of TEA, resulting in CIDNP formation.



These schemes demonstrate the possibility of the influence of exciplex on the CIDNP intensity. It is assumed then that the increase in CIDNP intensity with decreasing solvent polarity is caused by the growing yield of the exciplex.

According to Figure 7, the ratio between k_{exc} , k_{S} and k_{T} in the media of different polarity depends on the corresponding free energy changes ΔG_3 , ΔG_1 and ΔG_2 . One can expect that at low polarity, ($\epsilon < 20$) ΔG_1 , ΔG_2 , $\Delta G_3 < 0$ and $|\Delta G_3| < |\Delta G_2| < |\Delta G_1|$. In this case, the expected ratio between the rate constants will be $k_{\text{exc}} > k_{\text{T}} > k_{\text{S}}$, and the CIDNP sign of the TEA protons corresponds to the back electron transfer from S-RIP ($k_{\text{exc}} + k_{\text{S}} > k_{\text{T}}$). Otherwise, at higher polarity ($\epsilon > 20$), one can expect that ΔG_1 , $\Delta G_2 < 0$ and $\Delta G_3 > 0$ and $|\Delta G_2| < |\Delta G_1|$. Then $k_{\text{T}} > k_{\text{S}} > k_{\text{exc}}$, and the CIDNP sign of TEA will correspond to the recombination of T-RIP. Thus, the observed CIDNP effects and their dependence on solvent polarity can be attributed just to the inclusion of the exciplex (existing in equilibrium with RIP, $k_{\text{exc}} \sim k_{\text{S-T}}$) in the reaction scheme.

In addition this energy diagrams illustrate other possible contributions of the exciplex in the process of the NPX –PYR triplet population.

The analysis of the CIDNP effects on the N-methylpyrrolidine protons according to Kaptein's rules [27, 40] shows that for the intramolecular electron transfer, $k_{exc} + k_S > k_T$. Furthermore, as follows from the analysis, $k_S > k_T$ for the intramolecular PET within the entire polarity range, and $k_S < k_T$ for the intermolecular reaction. This ratio, $k_T > k_S$, is observed usually in the photoinduced reactions of aromatic hydrocarbons, like naphthalene, with amines [33]. Note that both of the *S,S* and *R,S* enantiomers manifest almost identical CIDNP effects for the entire polarity range.

Thus, the investigation of spin and magnetic effects in the photolysis of chiral NPX-PYR dyads results in the following conclusions. The appearance of CIDNP effects on dyad protons over the wide range of solvent polarity indicates that the intramolecular PET is involved in the quenching of the singlet excited states of the dyad. At the same time, the abovementioned results provide evidence for the participation of exciplex in this process. In particular, an increase in CIDNP intensity with decreasing solvent polarity and the very fast growth (20 ns) of the triplet state after laser pulse are compatible with triplet formation through the internal conversion into exciplex.

In conclusion, the exciplex appears to be the major source of triplet state population in the system under study, especially in solvents of low polarity, and may contribute to the stereodifferentiation in fluorescence quenching.

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Figure Captions:

Figure 1. Kinetics of the transient absorption of the NPX-PYR triplet state detected after laser pulse ($\lambda_{\text{obs}} = 440 \text{ nm}$).

Figure 2. Magnetic field dependence of the NPX-PYR triplet state yield after laser irradiation in acetonitrile (■) and tetrahydrofuran (Δ).

Figure 3. Dependence of the free energy of (a) pair of NPX radical anion and N-methylpyrrolidine radical cation and (b) exciplex formation on solvent polarity (ϵ). The dashed line denotes the energy of the excited singlet state of NPX.

Figure 4. NMR (a) and CIDNP (PSS) (b) spectra detected after laser irradiation of S,S-NPX-PYR (3 mM) in CD_3CN .

Figure 5. Dependences of the integral TR CIDNP intensity of N-methylpyrrolidine protons of (R,S) NPX-PYR dyad (10^{-3}M) on solvent polarity in the absence (●) and in the presence (○) of TEA (10^{-2}M). CIDNP of TEA protons (■) on solvent polarity in the reaction with dyad.

Figure 6. Dependence of TR CIDNP intensity of N- CH_2 protons of TEA on the solvent polarity in the reaction with naphthalene.

Figure 7. Energy diagrams of photoinduced processes in NPX-PYR dyad: (left) low polarity, (right) high polarity.

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