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Influence of the linking chain length on the recombination kinetics of covalently bonded triplet radical pairs and magnetic field effects

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Nanosecond laser flash photolysis technique is used to study the formation and decay kinetics of covalently linked triplet radical pairs (RP) formed after photoinduced electron transfer in the series of 21 zinc porphyrin—chain—viologen (Pph—Sp$_n$—Vi^{2+}) dyads, where the number of atoms (n) in the chain increases from 2 to 138. In poorly viscous polar solvents (acetone, $CHCl_3$—CH_3OH (1 : 1) mixture), the dependence of the rate constant of RP formation on n can be described by the equation $k_e = k_e{}^0 n^{-a}$ at $k_e{}^0 = 2.95 \cdot 10^8$ s^{-1} and $a = 0.8$. In the zero magnetic field, the RP recombination rate constant ($k_r(B = 0)$) is significantly lower than k_e and ranges from $0.7 \cdot 10^6$ to $8 \cdot 10^6$ s^{-1}. The dependence of $k_r(B = 0)$ on n is extreme. The dependence $k_r(B = 0)$ reaches a maximum at $n = 20$. In the strong magnetic field ($B = 0.21$ T), the significant retardation of triplet RP recombination is observed. The chain length has an insignificant effect on $k_r(B = 0.21$ T), which ranges from $0.3 \cdot 10^6$ to $0.9 \cdot 10^6$ s^{-1}. The regularities found are discussed in terms of the interplay of molecular and spin dynamics.

Key words: laser photolysis, porphyrin, viologen, magnetic field effect, electron transfer, triplet radical pair.

Reactivity of triplet radical pairs (RP) is due, to a great extent, to effects of spin dynamics.[1,2] These effects are pronounced in the recombination kinetics of RP formed during electron phototransfer between the excited photosensitizer molecule in the triplet spin state and the donor or acceptor molecule linked by the atomic chain.[3,4] The elementary step of RP formation occurs with the conservation of the total spin.[1] The recombination of the appeared triplet RP to diamagnetic products should include intersystem crossing, which, in particular, can efficiently be accomplished due to the coherent motion of electron spins induced by the electron-nuclear hyperfine coupling (HFC). Dynamics of these triplet-singlet (T—S) transitions is modulated by the external magnetic field due to the Zeeman splitting and the exchange interaction between unpaired electrons, which determines the energy gap between the singlet and triplet states of RP (2*J*).

In flexible covalently bonded RP, the *J* value depends on the distance and mutual orientation of the radical centers, which change during molecular motion, rather than on the chemical nature of the spacer.[5,6] Thus, the structure of the linking chain and molecular dynamics affect the spin evolution of RP, being a reason for several unexpected, at first glance, effects, which are observed for the recombination of bonded triplet RP.[3,4] They are: (1) an increase in the recombination rate of triplet RP with an increase in the polymethylene chain (n = 3—8) linking the radical centers, as it was observed for the acyl—$(CH_2)_n$—benzoyl and benzoyl—$(CH_2)_n$—benzoyl biradicals,[7,8] triplet RP of zinc porphyrin—$(CH_2)_n$—viologen dyads (Pph—Sp$_n$—Vi^{2+}),[9,10] and phenanthrene—$(CH_2)_n$—dimethylaniline,[11] benzophenone—$(CH_2)_n$—diphenylamine,[12] and benzophenone—$(CH_2)_n$—phenylphenol[13]; (2) a negative activation energy for the recombination of the triplet benzoyl—$(CH_2)_n$—benzoyl[8] and xanthone ketyl—$(CH_2)_n$—xanthenyl biradicals,[14] as well as triplet RP of Pph—Sp$_n$—Vi^{2+} in nonviscous media[10,15]; and (3) an increase in the recombination rate of triplet RP of the Pph—Sp$_n$—Vi^{2+} dyads with an increase in the solvent viscosity.[15—17] All these effects seem to be unexpected from the viewpoint of classical chemical kinetics (in the absence of spin effects) because an increase in the chain length linking radical centers, a temperature decrease, and an increase in the solvent viscosity must be accompanied by a decrease in the frequency of collisions of two ends of the flexible supramolecule and, hence, a decrease in the reaction rate.[18,19]

At the same time, analysis of published data showed that this "anomalous" (from the point of view of classical chemical kinetics) behavior of triplet RP of flexible supramolecules is not the only possible. It depends on the supramolecular structure (length of the chain linking the radical centers), properties of the medium (solvent viscosity), and the temperature and external magnetic field.[3] For example, the following regularities were found: (1) a decrease in the recombination rate with an increase in the chain length for the short triplet acyl—$(CH_2)_n$—benzoyl and ben-

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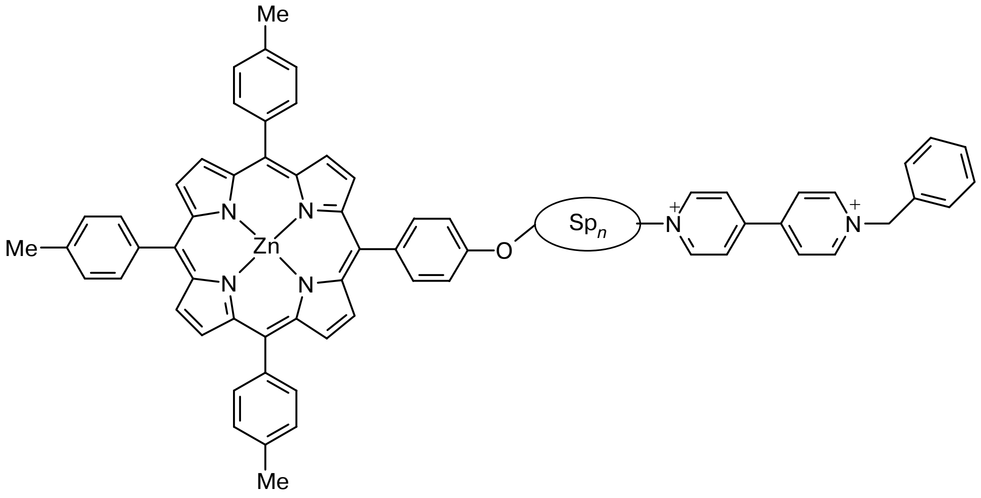
zoyl—$(CH_2)_n$—benzoyl biradicals[7,8]; (2) a positive activation energy at low temperatures, high viscosity, and strong magnetic fields during the recombination of the long triplet acyl—$(CH_2)_n$—benzoyl[20] and xanthone ketyl —$(CH_2)_n$—xanthenyl biradicals,[14] as well as for the recombination of triplet RP of Pph—Sp_n—Vi^{2+} in viscous media or in the strong magnetic field[10,15,21]; and (3) a decrease in the recombination rate with an increase in the solvent viscosity for triplet RP of the long Pph—Sp_n—Vi^{2+} dyads.[16]

In this report, we present for the first time the results on the kinetics of formation and recombination of triplet RP of the flexible Pph—Sp_n—Vi^{2+} dyads in which the chain length varies within very wide limits (the number of atoms n in the chain increases from 2 to 138 (Fig. 1)) in poorly viscous polar solvents (acetone and a methanol—chloroform mixture, 1 : 1 v/v). In the dyads with $n = 2$—16 porphyrin and viologen are linked by flexible polymethylene chains, and in the dyads with $n = 20$—138 the chains contain alternating polymethylene chains and 1,4-dioxyphenylene fragments (the length of each fragment was conventionally accepted to be equal to six). This choice of the chain structure simplifies substantially, from the one hand, the synthesis of dyads with $n > 20$ and, on the other hand, enables the retention of their flexibility. Preliminary studies of some dyads ($n = 3$, 6, and 10) showed that this series of supramolecules is promising for use because the pulse laser excitation of their solutions gives triplet RP in a high yield. These compounds have a undoubted advantage: a high photostability, and, hence, the photoseparation—recombination cycles are completely reversible under experimental conditions.

Experimental

Absorption spectra and kinetics of formation and decay of intermediate products were recorded on a nanosecond laser photolysis setup.[22] A PRA LN 102 dye laser was used as the excitation source (radiation wavelength 420 nm, pulse duration 0.5 ns) pumped by an N_2 laser (PRA LN 1000), which worked in a frequency mode. Kinetic curves were accumulated and averaged (usually by 128 laser pulses) using a Biomation 6500 high-speed analog-to-digital converter (USA) connected to a Pentium 200 PC. Each kinetic curve contained 1024 points, the distance between points being 2, 5, 10, or 20 ns, depending on the duration of the process. Kinetic parameters were determined by the nonlinear least-squares method using the Marquart algorithm. The data presented in the work are average values obtained by the processing of five kinetic curves for the indicated conditions.

In experiments with magnetic field, a quartz cell (cross section 8×8 mm) filled with a solution under study (0.5 mL) was placed between the poles of a permanent magnet. A change in the distance between the poles allowed the variation of the magnetic induction B from 0 (the magnetic field of the Earth, which is ~0.05 mT, was accepted as zero) to 210 mT (at the shortest distance between the poles). The cell was thoroughly



Sp_n	n
$(CH_2)_n$	2—14, 16
$(CH_2)_8$—OPhO—$(CH_2)_6$	20
$(CH_2)_8$—OPhO—$(CH_2)_{10}$	24
$(CH_2)_{12}$—OPhO—$(CH_2)_{12}$	30
$(CH_2)_{12}$—OPhO—$(CH_2)_{12}$—OPhO—$(CH_2)_{12}$	48
$(CH_2)_9$—OPhO—$(CH_2)_{12}$—OPhO—$(CH_2)_9$—OPhO—$(CH_2)_9$—OPhO—$(CH_2)_{12}$—OPhO—$(CH_2)_9$	90
$(CH_2)_9$—OPhO—$(CH_2)_{12}$—[OPhO—$(CH_2)_9]_2$—OPhO—$(CH_2)_{12}$—OPhO—$(CH_2)_9$—OPhO—$(CH_2)_6$	102
$(CH_2)_9$—OPhO—$(CH_2)_{12}$—[OPhO—$(CH_2)_9]_2$—OPhO—$(CH_2)_{12}$—[OPhO—$(CH_2)_9]_2$—OPhO—$(CH_2)_{12}$—OPhO—$(CH_2)_9$	138

OPhO =

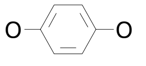


Fig. 1. Molecular structure of zinc porphyrin—viologen dyads.

evacuated before measurements to remove dissolved dioxygen. All experiments were carried out at 20 °C.

Dyads containing PF_6^- as the counterion were synthesized by a known procedure.[10,23] The synthesis of the dyads included the subsequent addition of dihaloalkyl, 4,4′-dipyridyl, and benzyl bromide to *meso*-4-hydroxyphenyl-tris(4-tolyl)porphine. Dihaloalkyls, $Br(CH_2)_nBr$ with n = 5, 7—9, 11—14, and 16, were kindly presented by Prof. K. Melbius (Institute of Experimental Physics, Berlin, Germany). To prepare the dyads with n > 16, the spacer was grown by the alternation of the reactions of the starting porphyrin with $Br(CH_2)_nBr$ and hydroquinone. All reactions were carried out in anhydrous DMF; toluene was added to enhance the solubility of compounds with long spacers. Reactions with the formation of an ether bond were carried out in the presence of anhydrous potassium carbonate. Substances were obtained at each stage in the chromatographically pure form. Uncharged compounds were chromatographed on silica using a heptane—toluene mixture as an eluent. Charged compounds were chromatographed on Sephadex LH-20 using acetone or methanol—chloroform mixtures as the eluents. The yield of target products at each stage was ≥70%. The obtained dyads are chromatographically pure substances, whose spectroscopic parameters correspond to the presented structures. Solutions with a concentration of $2 \cdot 10^{-5}$ mol L^{-1} were used for kinetic measurements.

Analyzing charge photoseparation and recombination, we performed calculations of the chemical kinetic problem using the program, whose algorithm has been described previously.[24] Since RP with different spin multiplicities and conformations do not differ by spectral parameters, the calculated time dependences of the concentrations of RP in different states were summated. The recombination rate constant obtained by the polyexponential analysis of the time dependence of the overall concentration of radical ions was compared to the experimental value.

Results and Discussion

Kinetics of formation and recombination of triplet RP. Electron phototransfer in the $Pph—Sp_n—Vi^{2+}$ dyads involves excited states of zinc porphyrin in both triplet (^3Pph) and singlet (^1Pph) excited states.[9,10,15—17,25] The relative contributions of the reactions involving ^1Pph and ^3Pph can be estimated from the relative fluorescence yield of the porphyrin (ϕ_{fl}), calculated as the ratio of integral fluorescence signals from the dyad and model zinc porphyrin, which is not linked to viologen.[10,15] The ϕ_{fl} value increases with an increase in n (at n = 2 $\phi_{fl} \le 0.01$, at n = 3 $\phi_{fl} \approx 0.1$; for the dyad with n = 10, ϕ_{fl} reaches 0.5).[10] Therefore, the contribution of electron transfer involving ^3Pph increases, and that involving ^1Pph decreases.

The reactions involving ^1Pph result in the formation of singlet RP, which, due to their short lifetime (<10 ns), cannot be observed by the nanosecond laser photolysis technique used in this work. These reactions predominate in the dyads with short chains.

Electron transfer in $^3Pph—Sp_n—Vi^{2+}$ results in the formation of triplet RP, whose absorption can be observed in the microsecond time interval at $n \ge 3$. Pulse laser excitation of $Pph—Sp_n—Vi^{2+}$ at n = 3—138 is accompanied in the nanosecond time interval by the formation of intermediates, whose yield increases with n, and the differential spectra correspond to the superposition of the spectra of the excited triplet state of Pph (λ_{max} = 470 nm) and radical pair $Pph^{+\cdot}—Sp_n—Vi^{+\cdot}$ (λ_{max} = 620 nm).[9,10,15] The typical kinetic curves of a change in the absorbance at these characteristic wavelengths are presented in Figs. 2 and 3.

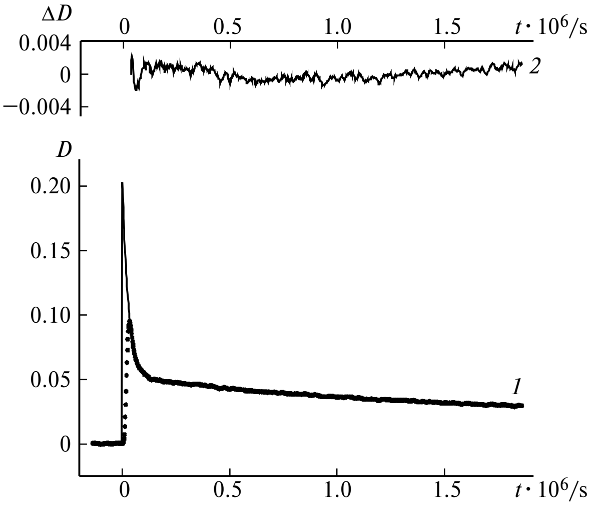


Fig. 2. Kinetic curve of changes in the absorbance (D) at 470 nm in the strong magnetic field (B = 0.21 T) detected after the pulse laser excitation of solutions of $Pph—(CH_2)_{12}—Vi^{2+}$ in acetone; points, experimental values of absorbance; solid lines (curve *1*), calculation by Eq. (2) at $k_e = 3.27 \cdot 10^7$ s^{-1}, $k_r(B = 0.21\ T) = 3.1 \cdot 10^5$ s^{-1}, $C_0 l = 3.39 \cdot 10^{-6}$ mol cm L^{-1}, $^T\varepsilon_{470} = 6 \cdot 10^4$ mol^{-1} cm^{-1}, $^R\varepsilon_{470} = 1.5 \cdot 10^4$ mol^{-1} cm^{-1}; *2*, corresponding deviations.

The change in the optical density at λ = 470 nm (see Fig. 2) is characterized by a fast increase in the signal within the time comparable to the resolution time of the technique (~10 ns) and the following decrease, whose kinetics is two-component with the characteristic times of the fast phase $1/k_e$ = 10—50 ns (remains unchanged when the external magnetic field is applied) and slow phase $1/k_r$ (being 120—1000 ns depending on n) in the zero magnetic field ($1/k_r(B = 0)$) and increases to 2—4 μs in the strong external magnetic field B = 0.21 T ($1/k_r(B = 0.21\ T)$). These results and the molar absorption coefficient of ^3Pph ($^T\varepsilon_{470}$) at 470 nm higher than that of RP ($^R\varepsilon_{470}$) allow us to assign the fast phase to triplet state decay and the slow phase can be attributed to the recombination of triplet RP.

At 650 nm the molar absorption coefficient of RP ($^R\varepsilon_{650}$) is higher than that of ^3Pph, hence, the fast increase in the absorbance with $1/k_e$ = 10—50 ns (distorted due to fluorescence of the porphyrin moiety) can be assigned to the formation of triplet RP due to the electron transfer from zinc porphyrin in the excited triplet state to viologen, and the slow decrease in the absorbance with $1/k_r$ = 120—1000 ns can be attributed to the recombination of triplet RP to form the ground state. Correspondingly, in the strong external magnetic

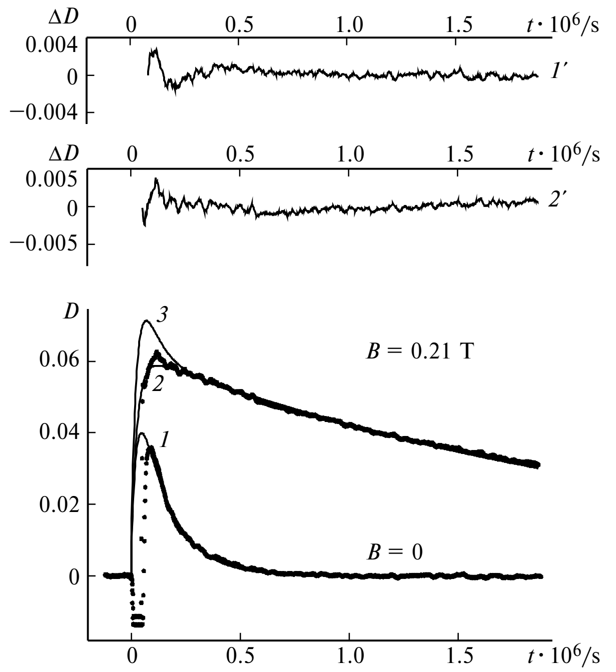


Fig. 3. Kinetic curves of changes in the absorbance (D) at 620 nm detected after the pulse laser excitation of Pph—$(CH_2)_{12}$—Vi^{2+} solutions in acetone. Points, experimental values of absorbance at $B = 0$ and 0.21 T. Curves *1* and *2* were calculated by Eq. (2), and curve *3* was calculated by Eq. (3). Parameters: $k_e = 4.11\cdot10^7$ s^{-1}, $k_r(B = 0) = 6.98\cdot10^6$ s^{-1}, $C_0l = 3.25\cdot10^{-6}$ mol cm L^{-1} (curve *1*); $k_e = 3.71\cdot10^7$ s^{-1}, $k_r(B = 0.21$ T$) = 3.8\cdot10^5$ s^{-1}, $C_0l = 3.61\cdot10^{-6}$ mol cm L^{-1} (curve *2*); $k_e = 3.71\cdot10^7$ s^{-1}, $k_r^0 = 1.2\cdot10^7$ s^{-1}, $k_r^{\pm} = 3.5\cdot10^5$ s^{-1}, $C_0l = 5.29\cdot10^{-6}$ mol cm L^{-1} (curve *3*); $^T\varepsilon_{620} = 3\cdot10^3$ L mol^{-1} cm^{-1}, $^R\varepsilon_{620} = 1.7\cdot10^4$ L mol^{-1} cm^{-1}. Curves *1′* and *2′*, deviations from experimental values for curves *1* and *2*, respectively.

field (0.21 T), the $1/k_e$ value remains unchanged, whereas $1/k_r$ increases to 2—4 μs (see Fig. 3).

The observed processes can be presented by the simple scheme

$$^3\text{Pph—Sp}_n\text{—Vi}^{2+} \xrightarrow{k_e} {}^3[\text{Pph}^{+\bullet}\text{—Sp}_n\text{—Vi}^{+\bullet}] \xrightarrow{k_r}$$
$$\longrightarrow \text{Pph—Sp}_n\text{—Vi}^{2+}, \qquad (1)$$

where ^{3}Pph—Sp$_n$—Vi^{2+} is formed within the characteristic time of the intersystem crossing ^{1}Pph → ^{3}Pph (~2.5 ns),[25] which is shorter than the resolution time of the detection system (10 ns). According to this, at times longer 10 ns, the time dependence of the induced absorbance is described by the equation

$$D_t = {}^TD_t + {}^RD_t = C_0l\{{}^T\varepsilon_\lambda\exp(-k_et) + {}^R\varepsilon_\lambda k_e[\exp(-k_et) -$$
$$- \exp(-k_rt)]/(k_r - k_e)\}, \qquad (2)$$

where ^TD_t and ^RD_t are the absorbances of ^{3}Pph—Sp$_n$—Vi^{2+} and ^{3}[Pph$^{+\bullet}$—Sp$_n$—Vi$^{+\bullet}$], respectively; C_0 is the effective concentration of ^{3}Pph—Sp$_n$—Vi^{2+} formed after the laser pulse and l is the effective optical path length, which are determined by the laser pulse energy and absorbance of the solution at the excitation wavelength. At a constant laser pulse energy, the C_0l product is constant for a specific sample. The corresponding values of the model unbonded system including zinc tetratolylporphine and benzylviologen were used as molar absorption coefficients of ^{3}Pph—Sp$_n$—Vi^{2+} and ^{3}[Pph$^{+\bullet}$—Sp$_n$—Vi$^{+\bullet}$] at 470 and 620 nm (see legends to Figs. 2 and 3). The quenching of the triplet state of zinc tetratolylporphine by benzylviologen in methanol results in the formation of the corresponding radical ions in a high quantum yield.[23] Thus obtained molar absorption coefficients agree well with the corresponding published data for close in structure compounds.[23,26]

Equation (2) describes satisfactorily the time dependence of the induced absorbance at the detection wavelength in the 440—800 nm range (see Figs. 2 and 3); the k_e, k_r, and C_0l parameters are independent of the detection wavelength, and the k_e and C_0l values are independent, in addition, on the external magnetic field.

To describe the recombination kinetics in the strong external magnetic field, we also verified a more complex model. Due to the Zeeman splitting, the ensemble of triplet RP decomposes to two subensembles, which represent the pairs obtained in the T_0 and $T_\pm$ states.[3,4] When the strong external magnetic field is applied, the $T_\pm \to T_0$ or S transitions, which occur due to HFC and paramagnetic spin relaxation, are retarded and, therefore, the pairs generated in the $T_\pm$ state recombine more slowly (rate constant $k_r^\pm$) than in the zero magnetic field ($k_r^\pm < k_r(B = 0)$). The pairs obtained in the strong magnetic field in the T_0 state still recombine with a high rate constant (k_r^0 is close to $k_r(B = 0)$). Under the assumption that the T_0 and $T_\pm$ states are populated with equal probabilities (according to published data,[27] these probabilities are $p_0 = 0.3466$, $p_+ = 0.3215$, and $p_- = 0.3319$), the time dependence of the induced absorbance is described by the equation

$$D_t = C_0l\{{}^T\varepsilon_\lambda\exp(-k_et) + {}^R\varepsilon_\lambda k_e[(\exp(-k_et) -$$
$$- \exp(-k_r^0t))/3(k_r^0 - k_e) + 2(\exp(-k_et) -$$
$$- \exp(-k_r^\pm t))/3(k_r^\pm - k_e)]\}. \qquad (3)$$

When processed the experimental data by Eq. (3), we used the values of $k_r^\pm = k_r(B = 0.21$ T$)$ and $k_r^0 = k_r(B = 0)$ obtained by analysis of the plots of D_t *vs.* t using Eq. (2) at $B = 0.21$ and 0 T, respectively. A fast component from the recombination of triplet RP born in the T_0 state appears in the kinetic curve (see Fig. 3, curve *3*) calculated by Eq. (3). A noticeable deviation of curve *2* (see Fig. 3) calculated by Eq. (2) is observed only in the initial region (0.1—0.4 μs), and experimental points are arranged between these curves. The distinction between the experimental and calculated by Eq. (3) data can be a result of distortions due to fluorescence and an insufficient resolution of the detection system, which disguises the contribution from the recombination of RP born in the T_0 state.[2–4]

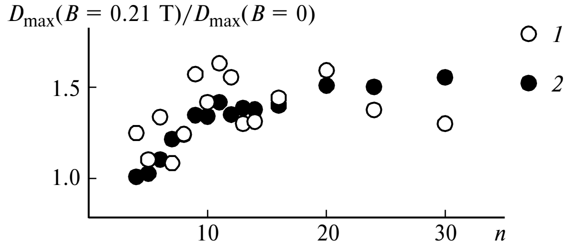


Fig. 4. Plot of the ratio of maximum values of the induced absorbance at 620 nm in the strong ($D_{max}(B = 0.21$ T) and zero ($D_{max}(B = 0)$) magnetic fields *vs.* number of units (n) in the chain linking porphyrin and viologen: experimental values (*1*) in acetone (n = 3—48) and $CHCl_3$—CH_3OH mixtures, 1 : 1 (n = 90—138) and values calculated by Eq. (2) using the experimental values $k_r(B = 0)$ and $k_r(B = 0.21$ T) (*2*).

A relatively slow, independent of the magnetic field, formation of triplet RP results in the experimentally observed increase in the maximum RP concentration under the magnetic field application (see Fig. 3). The value of this effect corresponds satisfactorily to the value calculated under the assumption that intramolecular electron transfer from the zinc porphyrin molecule to viologen occurs with the effective rate constant k_e and is the only channel of the formation of RP observed during experiment (Fig. 4).

Influence of the chain length linking radical centers on the kinetics of triplet RP formation. In poorly viscous polar solvents, the rate constant of RP formation (k_e) decreases monotonically with the number of atoms (n) in the chain linking the radical ion centers (Fig. 5, curve *2*). The observed dependence can be described by the equation

$$k_e = k_e{}^0 n^{-a} \quad (4)$$

at $k_e{}^0 = 2.95 \cdot 10^8\ s^{-1}$ and a = 0.8. It is of interest to compare this dependence with the frequency of collisions (k_{en}) of the donor and acceptor in the flexible supramolecules.

It is known that in the Pph—Sp_n—Vi^{2+} dyads electron transfer in the singlet electron-excited state occurs at almost each collision of the excited zinc porphyrin molecule and viologen fastened at the ends of the flexible chain (see below).[10,28] Thus, the k_{en} values can be estimated from analysis of the relative yields and lifetimes of fluorescence. These estimations, taking into account the known[10] values of ϕ_{fl} and fluorescence lifetime of unbonded zinc porphyrin, τ_s = 2.5 ns,[25] give $k_{en} = 4 \cdot 10^9\ s^{-1}$ (n = 3) and $4 \cdot 10^8\ s^{-1}$ (n = 10). For supramolecules in which zinc mesoporphyrin is linked by polymethylene chains with two viologen molecules, the k_{en} values calculated from the fluorescence lifetimes in methanol—acetone (1 : 1) mixtures are somewhat higher and equal[28] to $(1.7—2.7) \cdot 10^9\ s^{-1}$ for n = 9—14.

The above estimations of k_{en} for the Pph—Sp_n—Vi^{2+} dyads agree with published data for other systems (see, *e.g.*, reviews[18,19]). The numerical calculations using the Monte Carlo method for the generations of supramolecular conformations showed that the kinetics of collisions of the supramolecule ends with the polymethylene chains containing 10—20 units obeys the equation of first order with the rate constant k_{en}, which decreases with an elongation of the chain according to the equation similar to Eq. (4) ($k_{en} = k_{en}{}^0 n^{-a}$) at $a \approx 3/2$.[29] In these calculations, the frequency with which the supramolecular ends intersect the $4\pi r^2$ surface (where r is the distance at which the supramolecule ends entered into the reaction) was accepted as a collision frequency. Thus calculated k_{en} agrees well with the measured in methylcyclohexane quenching rate constant of fluorescence of anthracene linked with CBr_3 by the polymethylene chain of 11 units[30] and the rate constant of formation of pyrene excimers in the series of 11 supramolecules containing two pyrene molecules linked by the flexible chain with n = 6—28 (see Fig. 5, curve *1*)[31] and polysterene chains (n = 50—2000) in cyclohexane and toluene.[18,19,32] At 25 °C the $k_{en}{}^0$ value calculated by these data is $1.91 \cdot 10^{10}\ s^{-1}$, which is much higher than $k_e{}^0$.

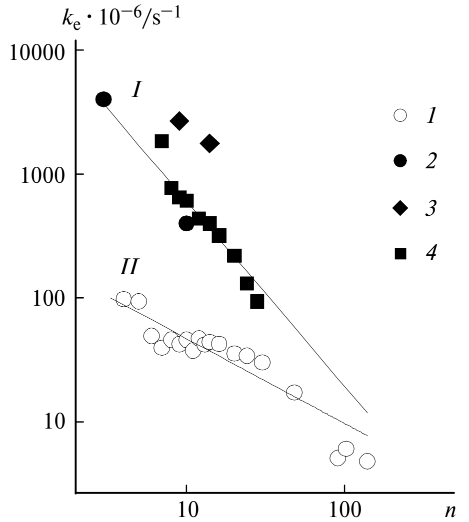


Fig. 5. Plots of the collision frequency of flexible supramolecular ends (k_{en}) (*I*) and rate constant of formation of triplet RP from porphyrin—viologen dyads (k_e) (*II*) *vs.* number of units (n) in the linking chain. Experimental k_e values (*1*) were measured in this work; k_{en} were published, see Ref. 10 (*2*), Ref. 28 (*3*), and Ref. 31 (*4*). Straight lines *I* and *II* were calculated by Eq. (4) at a = 1.5 and 0.8, respectively.

In the case of triplet RP formation, the molecular dynamics also plays an important role. This is indicated by a decrease in k_e with an increase in both the chain length (see Fig. 5) and solvent viscosity, which was observed for Pph—$(CH_2)_n$—Vi^{2+} (n = 6, 10) in methanol—glycerol mixtures.[16,17] At the same time, a comparison of curves *1* and *2* in Fig. 5 shows that the k_e values are much lower, especially for the dyads with short chains, than the k_{en} values estimated from the fluorescence measurements for Pph—Sp_n—Vi^{2+} and found by us in literature for other molecules. The difference between the k_e and k_{en} values can be explained under the supposition that, unlike the reaction of ^{1}P with Vi^{2+}, the transfer of an electron from ^{3}P to Vi^{2+} does not occur at each collision of the reactants. This is confirmed by the data for the unbonded system.[23] The anomalous plot of k_e *vs.* n can be a result of orientation effects appeared due to the fact that the electron matrix element, being one of the most important parameters that depends on the electron transfer rate, depends on the mutual orientation of the electron donor and acceptor rather than on the distance between them.[33,34] Since molecules of the electron donor and acceptor in the Pph—Sp$_p$—Vi^{2+} system are planar, a decrease in the chain length can favor the appearance of conformations with the unfavorable mutual orientation of the donor and acceptor. This effect can provide not so fast increase in k_e with a decrease in n as in the case of spherical reactants. The numerical calculations for chains with a finite size using the Monte Carlo method for the generation of conformations of molecules followed by counting of the ratio of the number of conformations in which the reaction occurs to the total number of conformations demonstrated[35,36] a possibility to decrease the power of n in Eq. (4) from 1.5 to 0.65.

Influence of chain length linking radical centers on the recombination kinetics of triplet RP. The plot of the recombination rate constant of triplet RP *vs.* chain length in the absence of the external magnetic field $k_r(B = 0)$ is presented in Fig. 6. A comparison of Figs. 5 and 6 shows that, in almost the whole range of n values, $k_r(B = 0)$ is much lower than k_e and becomes comparable with k_e only at high n. The plot of $k_r(B = 0)$ *vs.* n is complex. The $k_r(B = 0)$ value decreases on going from $n = 3$ to $n = 4$ but increases with the further increase in n reaching the maximum value at $n = 20$, and then it gradually decreases with an increase in n.

The recombination of triplet RP is substantially retarded in the strong external magnetic field (0.21 T). The chain length affects only insignificantly the $k_r(B = 0.21\ \mathrm{T})$ value (see Fig. 6). In the strong magnetic field, as well as in its absence, $k_r(B = 0.21\ \mathrm{T})$ decreases on going from the radical ion pair with $n = 3$ to the pair with $n = 4$. However, the further increase in n has almost no effect. As follows from Fig. 6, the magnetic effect $k_r(B = 0.21\ \mathrm{T})/k_r(B = 0)$ is maximal at $n = 20$.

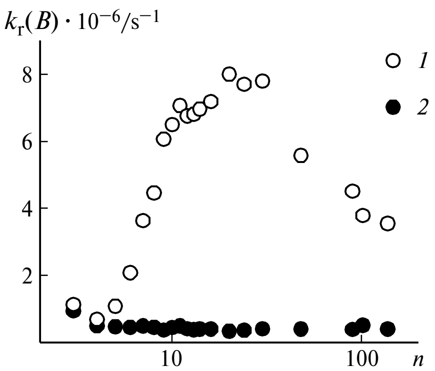


Fig. 6. Plot of the recombination rate constant of triplet RP (k_r) *vs.* number of units (n) in the chain linking porphyrin and viologen in the zero (*1*) and strong ($B = 0.21$ T) magnetic fields (*2*).

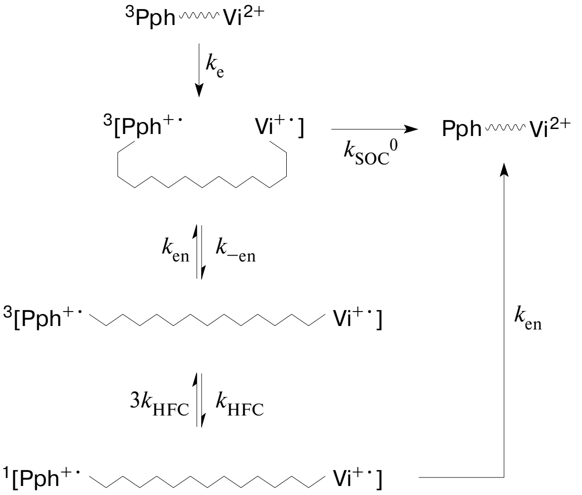


Fig. 7. Kinetic scheme of processes in triplet RP.

To describe the processes in the zero magnetic field (magnetic field of the Earth), we attempted to use the kinetic scheme presented in Fig. 7. According to it, intersystem crossing and conformational transitions are considered as reactions of first order with the corresponding rate constants. This approach is based on the fact that the interference of nuclear spin states in polynuclear systems simplifies substantially spin dynamics.[37—39] The exponential approximation of hyperfine coupling (HFC)-induced singlet-triplet (S—T) transitions has previously been used for the description of the temperature dependence of the recombination of the triplet acyl—(CH$_2$)$_n$—benzoyl[20] and xanthone ketyl—(CH$_2$)$_n$—xanthenyl biradicals[14] and recombination of triplet RP in micelles.[40]

In the absence of the external magnetic field, the isotropic HFC induces triplet-singlet (T—S) transitions in "open" conformations of RP in which the effective HFC (A_{HFC}) is higher than the exchange interaction ($2J$). Exchange interaction between radical centers was introduced in the framework of the simple model, according to which the exchange interaction occurs through solvent molecules.[41] According to this model, the J value decreases exponentially with an increase in the r distance

$$J = J_0\exp[-(r - R_0)/\beta_J], \qquad (5)$$

where J_0 is the averaged exchange interaction in the contact state at $r = R_0 = R_1 + R_2$ (R_1 and R_2 are the radii of reactants). In all calculations we used $J_0 = 1 \cdot 10^{10}$ rad s^{-1} and $\beta_J = 0.05$ nm.[42] The effective HFC value was calculated by the equation[38]

$$A_{HFC} = [\Sigma a_i^2 I_i(I_i + 1)]^{1/2}, \qquad (6)$$

where a_i and I_i are the HFC constants and spin quantum number of nuclei, respectively. Inserting the a_i and I_i for the radical cations of zinc tetraphenylporphine[43] and benzylviologen[44] into Eq. (6), we find $A_{\text{HFC}} = 2.5 \cdot 10^8$ rad s^{-1}. Using Eqs. (5) and (6), we can calculate the distance $r_j = 1.26$ nm at which A_{HFC} becomes equal to $2J$. This allows us to assign RP with the distance between the radical centers $r < r_j$ to an ensemble of RP in the "closed" conformation, and those with $r > r_j$ can be assigned to an ensemble of RP in the "open" conformation. Then we accepted that the conformational transition from the open to closed conformation occurs with the rate constant k_{en}. The rate constant of the conformational transition from the closed to open conformation ($k_{-\text{en}}$) can be calculated as $k_{-\text{en}} = D/r_j(r_j - R_0) = 6 \cdot 10^9$ s^{-1},[45] where D is the interdiffusion coefficient of the reactants calculated by the Stokes—Einstein equation ($kT(1/R_1 + 1/R_2)/6\pi\eta$) at $R_1 = 0.7$ nm and $R_2 = 0.36$ nm.[46]

The recombination of "closed" or contact triplet RP and T—S transitions in them also occur due to interactions independent of nuclear spins.[3,4,47] The main interaction of this type is spin-orbital coupling (SOC). This channel of RP recombination was taken into account by the introduction of the intersystem inverse electron transfer in the "closed" triplet RP with the first-order rate constant $k_{\text{SOC}}{}^0$ (see Fig. 7) and the corresponding channel of triplet RP decay with the rate constant k_{SOC}. Transitions induced by SOC are rather slow; nevertheless, they begin to make the main contribution[10,15—17,44,48,49] to the recombination of triplet RP in the strong magnetic field and in the case of RP with $n = 3$ and 4. The k_{SOC} value estimated for ^{3}[Pph$^{+\cdot}$—Sp—Vi$^{+\cdot}$] as $k_r(B = 0.21$ T) is virtually independent of n (see Fig. 6). The absence of the chain length influence on the lifetime in strong magnetic fields ($B \le 0.56$ T) has previously been found for triplet RP of supramolecules of the type phenanthrene—$(CH_2)_n$—dimethylaniline,[11] benzophenone—$(CH_2)_n$—diphenylamine,[12] and benzophenone—$(CH_2)_n$—phenylphenol.[13] A decrease in the chain length increases $k_r(B = 0.21$ T) only in the case of short chains (when n decreases from 4 to 3). The shortening of the lifetime of the short triplet acyl—$(CH_2)_n$—benzoyl and benzoyl—$(CH_2)_n$—benzoyl biradicals with a decrease in the chain length has previously been explained[7,8] by an increase in the efficiency of the SOC-induced T—S transitions.

When the above parameters are used, the calculated k_r values exceed much the experimental values, especially for the radical ion pairs with short chains (Fig. 8). In this situation, the agreement with experiment can be achieved by a decrease in k_{HFC} or $k_{-\text{en}}$. The calculations showed that, in the last case, $k_{-\text{en}}$ must be decreased to $4 \cdot 10^7$ s^{-1}. The radical ion pairs exist predominantly in the "closed" conformation ($k_{-\text{en}} \ll k_{\text{en}}$), which seems highly improbable in the absence of specific interactions between the radical centers. In fact, the radical cations of zinc porphyrin and viologen do not tend to form complexes in organic solvents.[9,10,15—17] Admittedly, hence, the effective (in the framework of the exponential approximation) k_{HFC} values are much lower than those calculated by Eq. (6). Only in the case of the recombination of RP with very long chains ($n \ge 90$) for which $k_{\text{en}} < k_{\text{HFC}}$, we can use the k_{HFC} value predicted by Eq. (6) (see Fig. 8). Thus, exponential approximation for HFC-induced transitions is invalid for fast conformational transitions with $k_{\text{en}} > k_{\text{HFC}}$.

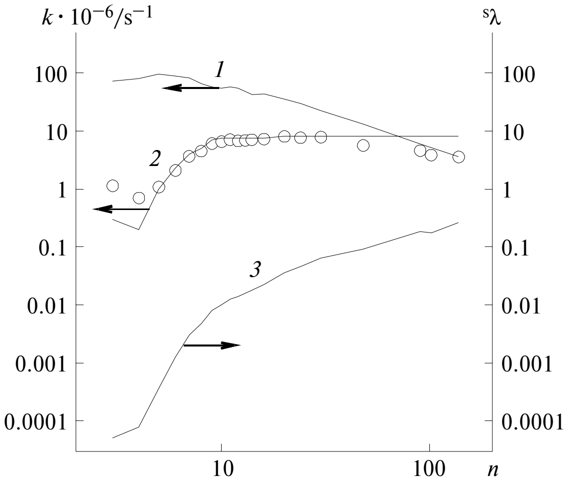


Fig. 8. Recombination rate constants of triplet RP in the zero magnetic field measured experimentally (points) and calculated by the scheme in Fig. 7 at k_e and k_{en} calculated by Eq. (4) at $a = 0.8$ and 1.5, respectively; $k_{\text{SOC}} = k_r(B = 0.21$ T); $k_{\text{HFC}} = 2.5 \cdot 10^8$ s^{-1} (curve *1*). Plot of k_{HFC} *vs.* n, which describes adequately the experimental data in the framework of the scheme in Fig. 7 (curve *2*). Plot of the value describing an admixture of the singlet state in triplet RP, $^s\lambda$ (see text) *vs.* number of atoms (n) in the chain linking porphyrin and viologen (curve *3*).

In terms of quantum-mechanical concepts,[48,49] HFC mixes different spin states of RP, due to which the T states gain the singlet character ($^s\lambda$). The product of $^s\lambda$ by k_{en} gives the rate constant of formation of diamagnetic products. To obtain the recombination rate constant k_r, k_{SOC} should be added to the $k_{\text{en}}{}^s\lambda$ value, *i.e.*, $^s\lambda = [k_r(B = 0) - k_r(B = 0.21 \text{ T})]/k_{\text{en}}$. The $^s\lambda$ value increases sharply with an increase in n from 3 to 9 (see Fig. 8). This effect is due to a decrease in the exchange interaction and, as a consequence, an increase in the efficiency of HFC-induced T—S transitions.[3,4] It is necessary to take into account the exchange interaction in radical ion pairs with $n = 3$—9, which follows unambiguously from the appearance of a maximum in the plots of $k_r(B)$ *vs.* magnetic induction, whose position (B_{max}) is a measure of the effective exchange interaction ($2J_{\text{eff}}$) in the pair.[3,4] We experimentally observed these maxima for ^{3}[Pph$^{+\cdot}$—$(CH_2)_n$—Vi$^{+\cdot}$] with $n = 3$—10; the B_{max} values being[10] 17, 3.8, and ~0 mT for $n = 3$, 6, and 10, respectively. The further smoother increase in $^s\lambda$, which is observed for RP with $n > 10$, cannot be related to a decrease in the exchange interaction because, in this case, the $2J_{\text{eff}}$ value is close to zero. This effect can be due[42,48,49] to the coherent nature of

HFC-induced spin evolution. A decrease in the collision frequency of radical centers results in the loss of coherency and an increase in HFC-induced T—S transitions.[42] In other words, the restrictions, which are imposed by the time scale of collisions of radical centers on the $\sin^2(A_{\text{HFC}}\tau)$ parameter describing spin evolution in the dynamic regime at short times, are eliminated with a decrease in k_{en}. Only in the systems with very long chains, at a low frequency of collisions of the radical centers, the states of RP gain the purely singlet or purely triplet character during first oscillations.[42,48,49] This regime, in particular, is characteristic of RP recombination in micelles with a long radius in which the collision frequency of the radicals is sufficiently low.[40]

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