Chem. Rev. 1993, 93, 537–570

Spin–Orbit Coupling in Free-Radical Reactions: On the Way to Heavy Elements

Igor V. Khudyakov, Yuri A. Serebrennikov,[†] and Nicholas J. Turro*

Department of Chemistry, Columbia University, New York, New York 10027

Received September 10, 1992 (Revised Manuscript Received December 1, 1992)

Contents

1. Introduction

The science of magnetic field effects (MFE's) in free-radical reactions has recently become a rapidly expanding area of chemical physics and physical chemistry (for reviews see refs 1–6). The development of the discipline has been driven by an unusual interplay of experiment and theory. The major theories of magnetic field effects exploit the concept of singlet–triplet transitions in geminate and random radical pairs and reveal how internal and external magnetic forces that operate on the pairs can be employed to design or interpret magnetic field effects on chemical reactions. One of the important and general magnetic forces that operate in radical pairs is due to spin–orbit coupling (SOC), which can serve both to induce or to quench magnetic effects on radical pair reactions.

Special interest in the role of SOC is related to the search for magnetic isotope effects (MIE's) on radical pairs containing atoms of elements heavier than carbon (up to uranium) and the potential application of separation of heavy isotopes through the MIE.

In this review the authors intend to provide a critical and comprehensive analysis of the role of SOC in radical-pair reactions, with emphasis on pairs containing heavy atoms. The literature reviewed is current to about mid 1992.

The next section is devoted to some general guidelines for consideration of SOC in quantum mechanical objects, which will be the basis for further analysis.

2. Spin–Orbit Coupling in Free-Radical Reactions. General Comments

2.1. SOC in Atoms

In an atom, two angular momenta, spin and orbital, contribute to the total electronic angular momentum. The interaction of these two momenta with each other is termed spin–orbit coupling (SOC). The origin of SOC may be viewed as arising from the interaction of the magnetic field associated with the spin angular momentum with the magnetic field associated with the orbital motion of the same electron in the electrostatic field of a nucleus. Most of the features of greatest physical significance can be deduced by inspection of the form of the operator for SOC in a hydrogen atom

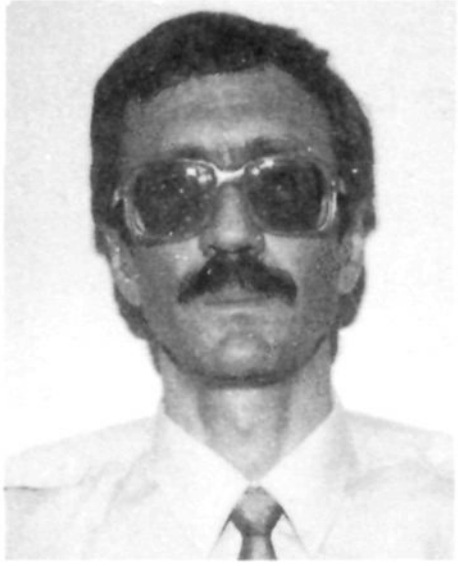
$$\mathcal{H}_{\mathrm{SOC}} = \xi_{n\ell}\ell\mathbf{s} \qquad (1)$$

where n is the principal quantum number and ℓ is the value of the orbital angular momentum. The value of $\xi_{n\ell} = 2\beta_e^2\langle Z/r^3\rangle_{n\ell}$ is termed the SOC constant for a specific $n\ell$ state of the atom, β_e is the Bohr magneton, ℓ is the orbital momentum operator, $\mathbf{s}$ is the spin momentum operator, r is the distance between an electron and a nucleus, and Z is the nuclear charge. In

---

[†] Present address: Department of Chemistry, University of Konstanz, D-7750 Konstanz, FRG.

0009-2665/93/0793-0537$12.00/0



Igor V. Khudyakov was born in Moscow, Russia, and graduated from the Chemistry Department of Moscow State University in 1971, after which he joined the staff of the Institute of Chemical Physics, Russian Academy of Sciences as a Research Fellow. He received the Ph.D. in 1975 and Doctor of Science Degree (D.Sc.) in 1984 from this Institute. Being a research advisor to a number of graduate students he became a Professor (1991, Diploma). He is a Titular Member of IUPAC. Since 1990 he has been a Postdoctoral Research Scientist at Columbia University with Professor N. J. Turro. His research interests include photochemistry, kinetics of fast reactions, reactivity of free radicals, and magnetic field effects in chemical reactions.

Yuri A. Serebrennikov was born in Odessa (the Ukraine) in 1954. He received his Ph.D. in Chemical Physics from the Institute of Chemical Kinetics and Combustion, Russian Academy of Sciences (Novosibirsk) in 1983, under Prof. A. I. Burshtein and Dr. S. I. Temkin. He moved to the University of Karaganda (Kazakhstan) to work as an Associate Professor in the Department of Quantum Chemistry where he directed two Ph.D. theses and nine M.S. students. Presently he is an Alexander von Humboldt Fellow at the University of Konstanz (Germany) with Prof. U. E. Steiner. The relationship between spin dynamics, molecular motion, and chemical reactivity in particular, in the role of magnetic interactions and spin relaxation in chemical kinetics, is the main subject of his research interests.

Nicholas J. Turro was born in Middletown, CT, attended Wesleyan University (A.B., 1960), and was an NSF Predoctoral Fellow with George S. Hammond at Caltech (Ph.D., 1963). After an NSF Postdoctoral Fellowship with Paul D. Bartlett at Harvard (1963–1964), he joined the Columbia University Chemistry Department where is now the Wm. P. Schweitzer Professor of Chemistry. His research interests include photochemical probes of interfaces, reactions in constrained environments, magnetic effects on reactions, and molecular recognition in photochemical reactions.

the hydrogen-like atom[7-9]

$$\langle 1/r^3\rangle_{n\ell} \sim Z^3/n^3\ell(\ell+1)(\ell+{}^1/_2) \qquad (2)$$

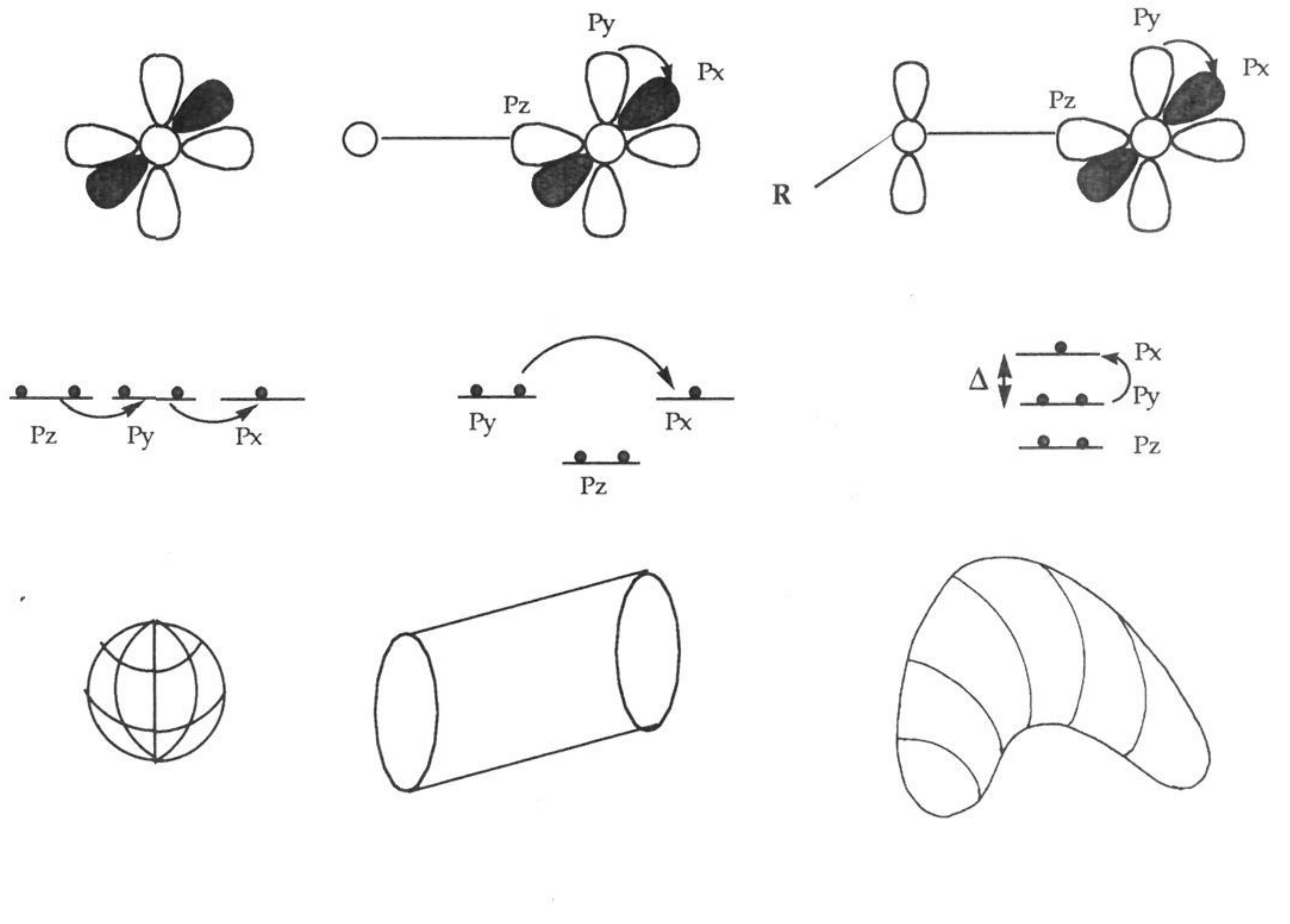
Therefore the SOC constant for hydrogen-like atoms is proportional to Z^4.[7-10] Such a dependence reflects the fact that as Z increases, the electron's orbit shrinks and the strength of the nuclear electric field increases. Both factors lead to a strong increase of the interaction of the electron's spin and orbital momentum and therefore to a strong increase in the energy of SOC in the system as Z increases. The SOC Hamiltonian (eq 1) takes into account only the interaction of spin and orbital angular momenta of the same electron and does not account for interaction with magnetic fields (MF's) due to orbital movements of other electrons in the many-electron atom. However, these interactions are usually accounted for by introduction of effective SOC constants for the valence electrons of atom A (ξ_A); the latter is determined from the atomic multiplet splitting.[7,11-13] Equation 3 is a generalization of eq 1 which has been successfully used for many-electron atoms.[7,8] In eq 3

$$\mathcal{H}_{\rm SOC} = \sum_i (\xi_A)_i \boldsymbol{\ell}_i \mathbf{s}_i \qquad (3)$$

the summation takes place over all electrons of atom A.

The action of SOC in atoms may be visualized by a simple example presented in Figure 1a. Transition of a p electron in a p^5 atom from a doubly occupied, say p_y, to singly occupied, say p_x, orbital, is accompanied by a simultaneous change of the orientation of the electronic orbital momentum, ℓ, i.e. ℓ_x to ℓ_y (Figure 1a). This orbital movement in the electric field of an atomic nucleus generates an internal magnetic torque acting on the spin of the p electron.

One of the clearest experimental manifestations of SOC in atoms is available in the fine splitting of atomic spectra. From such data the values of the SOC constant, $\xi_{n\ell}$, can be evaluated for hydrogen-like atoms and the magnitude of SOC for other elements of the periodic table can be compared, at least in a qualitative way, since there are a number of factors that must be considered, such as the nature of the orbitals involved in the actual SOC. Table I presents effective SOC constants, ξ_A, for the valence electrons of a number of atoms for the purposes of qualitative comparisons. From the data of Table I it is noted that the spatial distribution of electrons and the form of the orbitals determine the value of ξ_A, for many electron atoms. It is important to note that nuclear charge does not dominate the value of ξ_A. For example, for an atom of potassium ($Z = 19$) the ξ_A value is lower than that for nitrogen ($Z = 7$), and for uranium ($Z = 92$) ξ_A is lower than for bromine ($Z = 35$)!



(a) (b) (c)

Figure 1. Schematic representation of valence electron transfers leading to SOC: (a) atom (no excitation required); (b) diatomic molecule (no excitation required for transition between degenerate p_x and p_y AO's; (c) polyatomic molecule or radical (excitation is necessary to make a transition). Topology of chemical systems under consideration are also presented.

Table I. Effective Spin–Orbit Coupling Constants ξ_A (cm^{-1}) for a Number of Atoms[a]

element	C	N	O	Cl	K	Cr	Cu	Br	Mo	Ru	Rh	I
Z	6	7	8	17	19	24	29	35	42	44	45	53
ξ_A	28	76	151	586	38	223	828	2460	552	990	1212	5060

element	W	Re	Os	Pt	Au	Tl	Pb	U
Z	74	75	76	78	79	81	82	92
ξ_A	2089	2200	2500	4000	5091	7790	7800	2000

[a] Data of refs [12–18]. We avoid here a discussion of certain discrepancies in numerical ξ_A-values of the same atom presented in different publications.

The main reason for such deviation from the Z^4 dependence of ξ_A, which is valid only for hydrogen-like atoms, is the screening of valence electrons from the nuclear charge by the core electrons.

2.2. SOC in Molecules

In moving from atoms to molecules there is an important change in that the electrostatic potential, which switches from one that is spherically symmetrical for atoms to one that is anisotropic for molecules. After atoms, diatomic molecules possess the highest degree of symmetry (cylindrical or axial), so we consider them first.

2.2.1. Diatomic Molecules

In diatomic molecules, the electrons move in the axially symmetric electrostatic field of two nuclei (Figure 1b). The energies of p_x and p_y orbitals are equal and the electron can be envisioned to pass freely from one orbital to another. These transitions in the classical presentation of the phenomenon are equivalent to an electron rotation (orbital current) around the internuclear axis z. As a result, an intramolecular magnetic field directed along the z axis is created and this magnetic field interacts with the electron-spin magnetic moment.

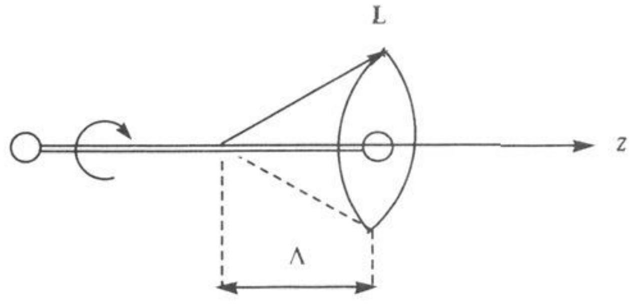


Figure 2. The electronic orbital angular momentum **L** precesses around the internuclear axis z in a diatomic molecule; the projection of **L** on the molecular axis is Λ.

The orbital angular momentum of an electron in a diatomic molecule precesses around the molecular symmetry axis in the same manner expected for a strong Stark effect (Figure 2). In this model the strong angular dependence of the electrostatic potential destroys the atomic spherical symmetry, which is required for the total orbital angular momentum **L** to be the constant of motion of the electrons. In other words, the operator $\mathbf{L}^2$ does not commute with the total electronic Hamiltonian $\mathcal{H}_e$ of the system. However, the operator $\mathbf{L}_Z$ does commute with $\mathcal{H}_e$, and this is the conserved quantity.

The z component of the orbital angular momentum $\mathbf{L}_Z$ is denoted Λ. States with different Λ are usually widely separated in energy due to the strong perturbation of electron orbital motion by the electric field along the internuclear axis. When the SOC energy is large compared with rotational distortion (Hund case a) the motion of the electron spin may be described as a precession about the axis defined by the two nuclei.[19] The component of the spin angular momentum $\boldsymbol{S}$ along the molecular axis is denoted Σ. Thus, in rotating linear molecules, corresponding to the case a, $\Omega = \Lambda + \Sigma$ is a constant of motion and one obtains an analogue of the known Russell–Saunders coupling scheme in the atoms. Due to SOC the energy of the orbitally degenerate state given by $\Lambda > 0$ is further divided into $2S + 1$ substates. The effect of SOC on the structure of spectra as well as on the designation of states in diatomic molecules is discussed in detail by Herzberg.[20]

It has been well established that SOC provides magnetic interactions, which lead to nonzero matrix elements between states of different spin multiplicity and thereby provides a mechanism which allows the corresponding electronic transitions to occur between states of different spin multiplicity.[7,12,21] Theoretical methods, which allow precise evaluation of radiative lifetimes of such transitions in diatomic molecules have been developed during the last decade, see e.g. refs 22–25. Since SOC can be rather large in heavy atoms, the extension of such theoretical methods to such systems as SeO[26] and MgO[27] seems to be very promising. It was shown that the magnitude of all SOC matrix elements are determined by the SOC in the heavy atom itself. For example, the matrix elements of the Breit–Pauli SOC operator (eq 4, see below) connecting lowest $X\,^2\Sigma^-$ term with higher states in the diatomic molecule containing a fourth row element, SeO, are 6 times larger than in the analogous molecule containing the third row element, SO.[26]

The most general expression for $\mathcal{H}_{SOC}$ for molecules used in practice is obtained under the postulate of the additivity of the Breit–Pauli Hamiltonian for two particles:[12]

$$\mathcal{H}_{SOC} = 2(\beta_e)^2\{\sum_{i,A} Z_A r_{iA}^{-3} \ell_{iA}\mathbf{s}_i - \sum_{i\neq j} r_{ij}^{-3}[\mathbf{r}_{ij}\times \mathbf{p}_i](\mathbf{s}_i + 2\mathbf{s}_j)\} \quad (4)$$

where $\mathbf{p}_i$, ℓ_{iA}, and $\mathbf{s}_i$ are the impulse, orbital, and spin angular momentum operators of i-th electron, respectively. Summation takes place over electrons (i) in all atoms (A).

Each term in eq 4 can be assigned a simple physical meaning. The first term is the sum of one-electron SOC in the Coulomb field of nuclei A. The second term is the interaction of electron spin i with the magnetic field induced by the orbital current of electron j (so called spin–other orbit interaction).

The electric field potential near the nucleus of atom A is controlled mainly by the contribution of an electric field of this atom, which has spherical symmetry. Therefore, the following simplified form of eq 4 is commonly adopted in the theory of SOC effects in diatomics:

$$\mathcal{H}_{SOC} = \sum_i \xi_{iA}(R)\ell_{iA}\mathbf{s}_{iA} + \sum_j \xi_{iB}(R)\ell_{iB}\mathbf{s}_{iB} \quad (5)$$

Here $\xi_{iA,B}$ is the effective SOC constant for i-th electron in atoms A and B; R is the distance between atoms. Such a one-center approximation for SOC Hamiltonian is rather standard and is well justified, see refs 7, 12, 21, and 28–31. The R dependence of ξ reflects the contribution of both atoms to the effective electronic potential and hence to the SOC. It is obvious that the functions $\xi_A(R)$ and $\xi_B(R)$ satisfy the boundary conditions:

$$\xi_{A,B}(R)_{|R\to\infty} = (\xi_{n\ell})_{A,B} \quad (6a)$$

$$\xi_A(R) + \xi_B(R)_{|R\to 0} = (\xi_{n\ell})_{AB} \quad (6b)$$

here $(\xi_{n\ell})_{AB}$ is the SOC constant in the united atom. It appears that the R dependence of $\xi_{A,B}$ is weak in homoatomic systems. Therefore, calculations of SOC, even in polyatomic organic systems, usually exploit the following one-electron operator:[7,21,22,28,29]

$$\mathcal{H}_{SOC} = \sum_A \xi_A \sum_i \ell_{iA}\mathbf{s}_i \quad (7)$$

where ξ_A is the effective SOC constant for the valence shell of A-th atom. The matrix element of the one-electron operator (eq 7) between singlet (S) and triplet (T) states is not zero if both states have different occupancies of two molecular orbitals (MO's), and these MO's includes different type atomic orbitals (AO's), e.g., p_x and p_y orbitals. One-center SOC integrals make a dominant contribution to the SOC energy in molecules. The anisotropy of SOC manifests itself in the dependence of matrix elements $\langle S|\mathcal{H}_{SOC}|T_i\rangle$ on the sublevels of fine structure of a triplet state ($i = x,y,z$).[7,21]

It should be noted, however, that in molecules with different atoms the increase of admixture of ionic (or charge transfer) structures with the R decrease often leads to the appearance of strong SOC from the corresponding ionic structures and the growth of the total SOC energy in the system.[7,21] This prediction is in a good agreement with the results of the rigorous calculations of the R dependence of $\langle ^3\Pi|\mathcal{H}_{SOC}|^1\Sigma^+\rangle$ matrix elements for KrO and XeO.[30,31] At the same time to our knowledge, there is no direct experimental verification of this hypothesis.

2.2.2. Polyatomic Molecules

The above considerations for spin–orbit coupling for diatomic molecules also apply in the main to linear polyatomic molecules. Figure 1 schematically demonstrates what happens to an atom with valence p electrons upon reduction of symmetry of the atomic system. The total electronic orbital angular momentum L can be conserved only in the case of a free atom possessing a degeneracy of orbitals (so that an electron can pass freely within the set of degenerate p orbitals, see Figure 1a). In the case of diatomic or linear polyatomic molecules only the projection of orbital momentum L, i.e., $L_Z = \Lambda$ is conserved (Figure 1b). However, for nonlinear polyatomic molecules, the orbital angular momentum is not preserved along any molecular axis (Figure 1c) so that the expectation value of any component of L equals zero. In such a case, which is by far the most common, the orbital angular momentum is said to be "quenched".

In this case, it would appear that for most molecules the orbital angular momentum would be zero. However, in the process of virtual or real valence electron transitions between states of different orbital symmetry, some transitory charge movement occurs. This movement of charge can be interpreted as the source of a "transition" orbital momentum and has analogy to an atom, where despite the absence of a permanent dipole momentum, electronic dipole transitions may occur between states of different parity as the result of an action of a "transition dipole moment". The orbital current arising from such transition moments creates an internal magnetic field which can be viewed as interacting with the electron spin magnetic momentum and thereby creates finite SOC in nonlinear molecules and other asymmetric polyatomic systems. The lower the amount of energy that is required for the corresponding orbital changes and the higher the charge of the nuclei in the vicinity of which this transition occurs, the larger the energy of SOC is in a system.

At the moment of transition, electron movement takes place in the anisotropic potential of nuclei and electrons forming the molecule. Hence, the energy required for the corresponding transition depends upon coordinates, and as a result SOC is anisotropic (see Figure 1). In fact, SOC reflects the symmetry of the atomic or molecular system: in an atom the SOC energy does not depend upon angular variables, but in a molecule, anisotropy of SOC is determined by the point group of a system.[7,12,21]

The energy gap between the ground electronic term and the closest excited state of different orbital symmetry, Δ, is an important characteristic of a system in determining the magnitude of SOC. The energy splitting Δ originates as a result of the action of the anisotropic interatomic Coulomb field. The latter can be, for example, a field of ligands surrounding central ion in a transition metal complexes (in such a case Δ corresponds to "ligand field splitting"), or it can be an intramolecular/intraradical electric field potential (in such a case Δ corresponds to "chemical splitting" resulting from the Coulomb interaction between closely packed atoms within a molecule). We will frequently inspect this parameter below, because the relation between Δ and ξ determines the magnitude and efficiency of SOC action in a system.[7,12,21] We note that the previous qualitative considerations based on a simple physical picture of SOC origination is confirmed by rigorous quantum mechanical calculations of SOC effects in polyatomic molecules.[7,12,21]

The most evident experimental manifestation of SOC in molecules is the violation of prohibition of S–T interconversion. The systematic examination of spectral manifestations of SOC in molecules, as well as the pertinent theoretical interpretation may be found in refs 7, 12, 13, and 21. A vast literature is devoted to the manifestation of SOC in photochemistry, see e.g. refs 9, 10, and 32.

Treatment of SOC according to eq 7 is valid not only for molecules (systems with closed electron shells) but also for open-shell systems such as polyatomic free radicals,[7,21,33] biradicals,[7,34] and transition metal complexes.[35,36]

2.3. SOC in Radicals and Radical Pairs

Spin–orbit coupling can have an effect on the spectroscopic properties of free radicals and on the reactivity of radical pairs undergoing combination reactions (coupling, disproportionation, and electron transfer). Of special interest to this report is the influence of SOC on the reactivity of radical pairs and on the magnetic field effects of radical pairs.

Table II. Some Energetic Characteristics of Small Inorganic Radicals X• [a]

radical X•	$N_3^\bullet$	•OH	NCS•	Cl	Br	I
ground electronic state of X•	$^2\Pi g$	$^2\Pi$	$^2\Pi$	$^2P_{3/2}$	$^2P_{3/2}$	$^2P_{3/2}$
ξ_A, cm^{-1}	71.3	140	320	587	2460	5060
$\xi_h \times 10^{-2}$, cm^{-1} [b]	1.2	1.5	3.9	5.9	24.6	50.6

[a] Data of refs 38 and 47. [b] $\xi_h = (\Sigma_A \xi_A{}^2)^{1/2}$ is the parameter characterizing the effective SOC of polyatomic radicals.

It is well known that SOC induces deviations of the value the g factor of a radical from that for the g factor of a free electron ($g_e = 2.0023$). This deviation from g_e in polyatomic radicals with quenched orbital momentum is proportional to ξ/Δ and increases in organic free radicals with heteroatoms ($Z > 6$), because, for these atoms, the SOC constant is much larger than for carbon atoms (cf. Table I).[33] (g factors of many free radicals can be found in ref 37.) The anisotropy of SOC in polyatomic systems causes a g-factor anisotropy which is well established by EPR measurements. As a result, the g factor of a free radical possesses the characteristic of a tensor, $\mathbf{g}$.

In most organic free radicals, the orbital angular momentum is quenched. However, in certain inorganic free radicals an orbital degeneracy exists and hence "unquenched" electronic angular momentum **L** is preserved. Such cases are represented by atomic free radicals (Cl•, Br•, I•) or small inorganic linear free radicals $N_3^\bullet$, •OH, •NCS. In such cases the value of the free radical g factor deviates strongly from the value for g_e. The presence of a large internal magnetic field due to strong SOC leads to a large value of a doublet splitting ξ_h for such radicals (see Table II).

A strong deviation of the value of the g factor from g_e is also observed for a number of transition metal complexes with a large nuclear charge and symmetrical ligand structures which lead to partially unquenched orbital angular momentum of electrons in partially filled d and f electronic shells. For example, for radical cations of $Ru(bpy)_3{}^{3+}$ $g_\parallel = \pm 1.14$, $g_\perp = 2.64$[39] and for $UO_2{}^+$ two sets of g-factor main values were obtained from ESR spectra $g_\parallel = 0$ (1.3), $g_\perp = 2.5$ (1.97).[40]

Let us now consider two free radicals which may be considered as behaving as a radical pair. We may conditionally divide radical pairs into two types: contact and spatially well-separated radical pairs (RP's). We shall define *contact* RP's as those which are positioned at $\rho < R < \rho + \Delta_c$, where ρ is the sum of van der Waals radii, Δ_c is the increase of the distance between radicals, where the electron exchange integral decreases e times (usually from one to several angstroms[1,41]), cf. Figure 3. *Spatially-separated* RP's are those positioned at $R > \rho + \Delta_c$ (usually 5 Å or greater). In most cases it is possible to consider *spatially well-separated* RP's as those positioned at $R \gg \rho + \Delta_c$ (Figure 3).

A pair of atomic radicals represents the simplest RP. The recombination of iodine and bromine atoms has attracted considerable interest and has been investigated for decades, see for review ref 42. Recently, picosecond studies of the cage effect under photodis-

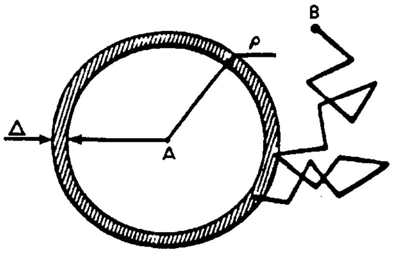


Figure 3. Kinetmatic scheme for an elementary act of liquid-phase reaction between free radicals, see text for discussion. The dashed line represents the Brownian path of reactant B.[1]

sociation of molecular bromine and iodine into atoms have revealed the limited application of the diffusional model for the description of the cage effect in a condensed phase.[42] This limitation has a rather simple physical origin. The spatially well-separated iodine or bromine atoms in their $^2P_{3/2}$ states constitute 4 × 4 electronic states of atomic RP. These states correlate with different molecular terms, but only a doubly degenerate state (A, A′) and the ground molecular state X are in a potential well with depth larger than k_BT at room temperature. It has been shown that the transient trapping within A and A′ states prior to formation of the final product X gives rise to an unexpectedly long time for recombination into the X state.[42] In fact, at rather short separations between iodine atoms, an activation by coupling to the orbital motion is required to overcome the splitting between the surfaces,[42] which leads to a relatively long time of geminate recombination.

When the interatomic distance $R > 5$ Å the energy gap between molecular terms becomes smaller than k_BT, the transitions between electronic terms can be caused by the relaxation of the projection of the atomic electronic angular momentum, $\mathbf{J} = \mathbf{L} + \mathbf{S}$, along the internuclear axis.[43] This process is analogous in a sense to the incoherent S–T transitions between the states of a polyatomic geminate RP induced by spin lattice relaxation.[1,4] Thus, strong internal SOC in an *individual* species constituting the geminate RP may determine the reaction pathway even at the stage of spatially well-separated RP's.

Very recently it has been shown by rigorous quantum chemical calculations[44] that matrix elements of Breit–Pauli Hamiltonian (eq 4) between the singlet and lowest triplet state of H_2O_2 increase on the way to dissociation limit, i.e. with the increase of O–O distance R_{O-O} and production of $^{\bullet}OH + {}^{\bullet}OH$ radical pair. The estimations of the transition probability, P, of $\tilde{A}{}^1A \rightarrow {}^3B$ intersystem crossing show that this quantity sharply increases with R_{O-O} increase:[44]

P	R_{O-O}, Å
0.019	2.0
0.12	2.5
0.44	3.0

Moreover, for $R_{O-O} > 3.5$ Å the exchange interaction and thus the energy gap between molecular terms becomes smaller than the SOC in the hydroxyl radical. Thus, as in the case of atomic radicals, the strong internal SOC in $^{\bullet}OH$, or in other axially symmetric species should govern the recombination pathway on the stage of spatially well-separated RP's (see also discussion at the end of section 5).

However, in polyatomic free radicals with quenched orbital momentum the energy gap Δ between states of different orbital symmetry is, as a rule, much higher than that for a united or closely coupled systems (such as contact RPs, exciplexes) or even in molecules, where Coulomb interaction between different chemical groups is lower than within such closely coupled chemical groups. As a result the energy splitting Δ between MO's of united system should be lower than in a free constituent of such a united system. This fact, in particular, explains the exponential decay of the matrix elements of SOC between S and T states of a RP when the interradical distance R increases[45,46] (see also section 2.4).

The concept of a rapid decrease of the SOC matrix element between S and T states of a RP as the interradical distance increases is deep seated. However, this statement is strictly correct only for RPs consisting of only orbitally nondegenerate radicals with quenched orbital momentum!

It has been noted that strong "intraradical" SOC (IRSOC) may determine the intersystem crossing (ISC) rate in a closely coupled RP system (e.g., triplet exciplex, contact RP).[38,47,48] The formation of a contact pair of radicals, in which at least one of them has large SOC, may result in additional removal of orbital degeneracy and thus diminish SOC energy in a coupled system. It is obvious that for such systems the expected exponential decrease of SOC with the interradical distance increase does not strictly apply.

In individual free radicals or in closely coupled RP systems strong IRSOC mixes different spin–orbital states. As a result, the α and β electron spin functions used to describe the spin state of organic radicals must be replaced by strongly "spin–orbit-mixed Kramers doublet" components α' and β'.[5,49] Consequently, the spin states of such a RP corresponds to a mixture of "pure" configurations with $S = 0$ and $S = 1$.[5,49,50]

For example, it has been already mentioned that due to the strong SOC the **g** tensor of $Ru(bpy)_3^{3+}$ ground state is highly anisotropic and its principal values strongly deviate from g_e. Correspondingly, the components α' and β' of the lowest Kramers doublet (the effective spin quantized along the trigonal axis of the $Ru(bpy)_3^{3+}$ complex of D_3 symmetry) have about an equal contribution of "normal" α and β spin functions.[36,49,50]

The considerations presented above have a clear physical basis. Despite this fact it has been stated quite recently that the conventional theory of spin-dependent recombination of spatially-separated RP's requires generalization in the case of particles with strong internal SOC.[5,49–51]

2.4. SOC in Biradicals

We shall consider the effect of SOC on the chemical behavior of biradicals for which the odd electron centers are held together by a flexible chain or by a rigid bridge. There are numerous analogies between a contact and slightly separated radical pair and a biradical in which the odd electron centers are connected by a flexible chain. An important difference is that the dynamics of the electronic and magnetic interactions between the odd electrons in such a biradical are modulated by the flexible chain dynamics, whereas the dynamics of the electronic and magnetic interactions between the odd electrons in a radical pair are modulated by the random diffusional motions of the two free radical fragments in the medium in which they are immersed.

An important qualitative theoretical interpretation of SOC in biradicals was presented for the first time by Salem and Rowland[52] in 1972. The analysis carried out in this pioneering publication produced the following conclusions: (i) the SOC energy in biradicals sharply decreases with the separation distance R between radical centers and increases as the angle φ between two AO's occupied by single electrons approaches 90°; and (ii) the SOC energy in biradicals is proportional to zwitterionic character of the singlet state of the system.[52] These qualitative predictions are based on the physical picture of the SOC phenomenon presented above and have been completely confirmed by ab initio calculations of biradicals.[45,46] It has been shown that the dependence of the matrix element of the SOC operator between S and T states of the trimethylene biradical $^\bullet CH_2CH_2CH_2{}^\bullet$ and that of the pair of individual methyl radicals on R and mutual orientation of corresponding p orbitals is well described by the following semiempirical formula:[46]

$$|\langle S|\mathcal{H}_{SOC}|T\rangle| \approx \exp(-R/\Delta_c)\sin\varphi \qquad (8)$$

Here $\Delta_c = 0.33$ Å, φ is the angle between p orbitals localized on the radical centers. The calculations of ref 46 show that the coupling interaction which occurs through the chemical bonds in the biradical increases SOC energy by 2.5 times compared to that in individual methyl radicals.[46]

The calculations made in refs 45 and 46 are important, because they create a quantitative basis for understanding the effect of SOC on intersystem crossing processes in reactive systems—biradicals, exciplexes, etc. In particular, the distance (R) dependence of the SOC matrix element explains the experimental results of ref 53. SOC contribution into intersystem crossing in biradicals is 76%, 86%, and 94% in the Earth's field for 1,12-, 1,11-, and 1,8-biradicals, respectively.[53]

3. Spin-Orbit Coupling as the Interaction Responsible for Magnetic Field Effects

In this section and sections 4 and 5 we shall consider the experimental manifestation of SOC in magnetic and spin effects studied by different experimental techniques, the most important of which are magnetic field effects (MFE's) on chemical reaction rates and cage escape values, chemically-induced dynamic nuclear polarization (CIDNP), chemically-induced dynamic electron polarization (CIDEP) and stimulated nuclear polarization (SNP).

3.1. Magnetic Field Effects in Photochemical Reactions Involving Paramagnetic Intermediates

Most photochemical reactions involve paramagnetic intermediates (radicals, radical pairs, biradicals, triplets, etc.) at a critical rate- or product-determining stage. In general, some aspect (ratio of products, efficiency of reactions, kinetics of formation and decay, etc.) of the course of the reaction may be varied by the application of an external field if the field causes a change in the spin dynamics at a critical stage of a photochemical sequence. The magnitude of the magnetic field effect (MFE), the sign of the MFE relative to the result at zero field, and the detailed magnitude of MFE as a function of varying magnetic fields are all important clues to the mechanism of the MFE. In this report, we are mainly concerned with MFE's that are brought about by the operation of effective spin-orbit coupling (SOC) in a paramagnetic intermediate in a photochemical reaction. To systemize our approach, we first define MFE in a simple operational sense that is easy to relate to an experiment. Then we propose two major mechanisms in which SOC can lead to a significant MFE in photochemical systems. In the following sections (sections 4 and 5), we analyze the mechanisms by which SOC can operate to "promote" or to "quench" the MFE of paramagnetic intermediates.

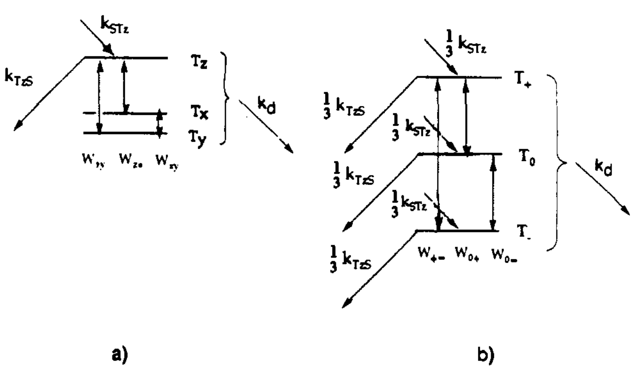


Figure 4. Schematic representation of the triplet mechanism of MFE: (a) zero-field case, (b) magnetic field mixing of zero-field triplet sublevels. In case a only T_z sublevel is populated under S → T interconversion (rate constant k_{ST_z}) and is depleted by SOC-induced T → S interconversion into the singlet ground state of reaction products (rate constant k_{T_zS}). k_d is the rate constant of the triplet exciplex dissociation into free radicals; W_{ij} stands for the relaxation rate between ZFS sublevels (a) and between high-field triplet eigenstates (b).

Since most of the investigations of MFE assume the radical pair (or biradical) paradigm as a working basis to examine the relevant experimental data, we shall define the *relative* magnetic field effect in a chemical reaction in terms of the ideas of the efficiency of the "cage effect" or the efficiency of "radical pair escape" from a cage. A useful parameter, A, readily related to measurable experimental concentration is given in eq 9, where here and below e_B (e_0) is the radicals escape (or yield) in a solvent bulk in the presence (absence) of the external field B, C_B (C_0) is the initial concentration of radicals which leave a cage (or are formed), and e is

$$A = (e_B - e_0)/e_0 = (C_B - C_0)/C_0 \qquad (9)$$

the fraction of produced radicals, which escaped the cage. The concentrations C_B (C_0) can be readily measured by the technique of laser flash photolysis.

3.2. Triplet Mechanism

The anisotropy of SOC, which was discussed in section 2, leads to a high selectivity of the interconversion between molecular singlet and triplet sublevels. The rates of population (k_{ST_i}) and depopulation (k_{T_iS}) vary greatly among the different zero-field triplet sublevels, T_x, T_y, and T_z,[7,12,21] cf. Figure 4a. This selectivity is preserved in the presence of an externally applied magnetic field. After selective population has occurred, the spin-lattice relaxation (SLR) drives the spin distribution over the triplet sublevels to thermal equilibrium. Obviously, significant nonequilibrium population of the triplet manifold takes place when the rates of selective population (from an excited singlet state, S_1) and decay (into the singlet ground state S_0) processes, caused by SOC anisotropy, are higher than the SLR rates (W_{ij}) in a triplet molecule, exciplex, etc., cf. Figure 4a. When this triplet molecule or intermediate participates in a chemical reaction with formation of a RP, the nonequilibrium spin population can be transferred to the radicals and manifests itself in a polarization of the ESR spectra. *The selective overpopulation* or *the selective depletion of triplet sublevels in an intersystem crossing step* is the essence of the so-called triplet mechanism (TM) of free-radical electron polarization formation suggested by Wong, Hutchinson, and Wan[54a] and by Atkins and McLauchlan.[54b] Below we shall employ the term TM as the mechanism responsible for certain phenomena involving a magnetic field dependence.

Considerable experimental data has been compiled and systematized in refs 1, 3, and 55–57 which testify that TM is an important source of nonequilibrium electron polarization of radicals formed during the photolysis of aromatic and aliphatic carbonyl compounds. It is worthwhile to mention that nonequilibrium polarization of triplets may result in nonequilibrium nuclear polarization due to electron–nuclear hyperfine coupling (HFC). This possibility should be taken into account in the interpretation of CIDNP experiments.[1,58]

Further, SOC-induced spin-selective decay of triplet sublevels (i.e. decay with different rates) can lead not only to the creation of a nonequilibrium spin population in a system. The rate of mixing of zero-field triplet sublevels which occur by the Zeeman interaction obviously depend upon external MF. This effect of MF leads to the dependence of the observed T-state lifetime τ of an exciplex or of a contact RP upon the flux density B of an applied external magnetic field and, therefore, will influence the probability that a solvent-caged primary geminate radical pair will escape into solvent bulk. For the initially uniform population of triplet sublevels, the overall $T \rightarrow S_0$ interconversion may become more efficient in a field, and one should expect a reduction of τ, and therefore a diminishing of the free-radical escape in a field, see Figure 4a,b.

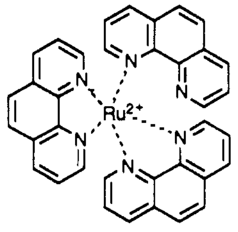
As a result for systems with an initially uniform population of triplet sublevels (exciplexes, contact RP's), the triplet mechanism always leads to a negative MFE ($A < 0$).

In radical reactions this phenomenon has been observed for the first time and has been provided with an adequate interpretation in the publications of Steiner and coauthors.[59,60] These authors have studied the influence of an external magnetic field on the efficiency of yield, e, of radical ions, generated from exciplexes formed by triplet thionine and a number of halogen-substituted anilines. A strong dependence of e upon the position of a heavy atom in the aniline molecule and a systematic increase of the absolute values of negative magnetic field effect with the increase of a nuclear charge Z in the substituent has been observed.

The significant negative MFE (the radical escape was 20% less in a field of $B = 1.5$ T) was found in a nonviscous solvent (benzene, $\eta = 0.59$ cP) for the thionine/*p*-iodoaniline system.[59,60] It was proposed that a triplet mechanism (SOC-induced selective $T \rightarrow S$ interconversion within the corresponding exciplex) is responsible for the observed magnetic field effect. The system has been investigated in greater detail, and a quantitative agreement between theory and experiment was achieved.[60]

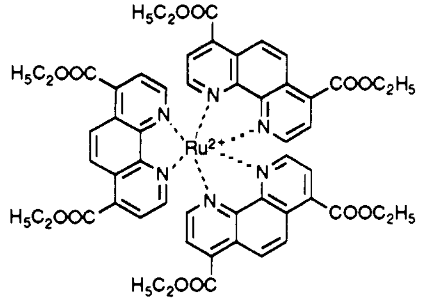
Similarly, a triplet mechanism has been proposed to explain the MFE observed in electron-transfer photoreactions in the following systems: erythrosine–*N,N'*-methyl viologen (denoted as MV^{2+}),[61] Methylene Blue–*p*-iodoaniline,[41] and tris[4,4'-bis(ethoxycarbonyl)-2,2'-bipyridyl]ruthenium(II) (denoted as $Ru(dce)_3^{2+}$)–*p*-iodoaniline.[49,51] Structural formulae of $Ru(dce)_3^{2+}$, MV^{2+} as well as that of tris(2,2'-bipyridyl)ruthenium(II), $Ru(bpy)_3^{2+}$, are as follows:

$Ru(bpy)_3^{2+}$



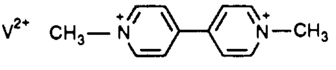
tris(2,2'-bipridyl)ruthenium(II)

$Ru(dce)_3^{2+}$



tris[4,4'-bis(ethoxycarbonyl)-2,2'-bipiridyl]ruthenium(II)

MV^{2+}



N,N'-dimethyl viologen

The latter example is instructive in the sense that a MFE on photoreduction of $Ru(dce)_3^{2+}$ has been found *only in the case when the donor was the compound with the largest SOC* within the row of compounds used, namely *p*-iodoaniline.[49] The data obtained in this work unambiguously show a systematic decrease of radical-ion yield e_0 with increase in nuclear charge Z of the halogen substituent. For example, e_0 (*p*-iodoaniline)/e_0(aniline) equals 0.12.[49] This effect depends also upon the position of the heavy atom in the aniline molecule, in particular, e_0(*o*-iodoaniline)/e_0(*p*-iodoaniline) = 1.83. The important peculiarity of these results is the following: SOC associated with the radical $Ru(dce)_3^+$ is not sufficient to induce a TM MFE despite the presence of the heavy atom Ru ($Z = 44$).[49]

The main ideas and main stages of MFE calculations within the framework of the TM are described in detail elsewhere.[4,5] Therefore, we shall confine ourselves to a brief review of publications devoted to the theory of the TM.

The solution of kinetic equations for the density matrix enables one to derive the main characteristics of the triplet system from experimental data, namely the triplet-state lifetime τ, the relative A (see eq 9), and the initial electron polarization P[62], for details see refs 59, 60, and 63–71.

The obtained experimental results may be explained by consideration of the two following alternative sources of a nonequilibrium spin population of a triplet precursor of the RP: (i) The T state is populated in a spin-substate selective process, but its decay is supposed to be the same for all the triplet spin sublevels.[63-68] (ii) The T-state decay is a sublevel selective process, but its initial population is not.[59,60,69] The analysis of a general case can be found in refs 70 and 71.

The general conclusion of these publications is the following: in solvents of low viscosity ($\eta \sim 1$ cP) the magnitude of the observed MFE cannot be large ($|A| = 1$–10%) due to fast SLR between triplet sublevels, which results in the suppression of MFE. The results of calculations of ref 69 for the case of equal initial populations of triplet sublevels show that in nonviscous solvents the value of the relative, A, is given by

$$A = -(^2/_3)(\omega_0/k_1)^2(D_k^2 + 3E_k^2)/(D^2 + 3E^2)(1 + k_0T_1) \quad (10a)$$

provided the following condition holds true:[71]

$$1 \gg \epsilon^2 = [D/(\omega_0 + 3k_1) + D_k/3k_1]^2 \quad (10b)$$

Here D and E are the zero-field splitting (ZFS) parameters of triplet sublevels, and the other parameters have the following meaning:

$$D_k = (k_{T_xS} + k_{T_yS})/2 - k_{T_zS} \qquad E_k = (k_{T_yS} - k_{T_xS})/2 \quad (11a)$$

$$k_0 = k_d + (\sum_i k_{T_iS})/3 \quad (11b)$$

$$k_1 = k_0 + 1/\tau_{\theta 2} \quad (11c)$$

The rate constants k_{T_iS} and k_d determine the rate of SOC-induced deactivation of triplet sublevels and the rate of triplet RP formation, respectively (cf. Figure 4); $\tau_{\theta 2}$ is the orientational correlation time for a second-rank tensor.[72] In the case of isotropic rotational diffusion $\tau_{\theta 2}^{-1}$ equals $6D_R$ (D_R is the rotational diffusion coefficient) and may be estimated according to the Stokes–Einstein–Debye formula:[72]

$$\tau_{\theta 2} = 4\pi r^3\eta/(3k_BT) \quad (12)$$

Here r is the hydrodynamic particle radius.

Parameters D_k and E_k describe the anisotropy (sublevel selectivity) of SOC-induced decay of triplet into the singlet ground state. When magnetism due to orbital angular momentum is absent ($L = 0$), the rate of longitudinal relaxation induced by reorientations of a triplet in nonviscous media is described by the following formula:[65,69]

$$1/T_1 = [2(D^2 + 3E^2)/15k_1] \times \left[\frac{1}{1 + (\omega_0/k_1)^2} + \frac{4}{1 + (2\omega_0/k_1)^2}\right] \quad (13)$$

The characteristic feature of the TM is that the MFE (in a nonviscous solvent) saturates in the high field ($\omega_0 \gg k_1$), when the Larmor frequency exceeds the sum of the dissipative rate constants k_0 and $\tau_{\theta 2}^{-1}$. In solvents of low viscosity the maximum value of MFE according to the TM is

$$A_{max} = -8(D_k^2 + 3E_k^2)/45k_0k_1 \quad (14)$$

(For the meaning of parameters in eq 14 see eq 11.)

For the majority of organic molecules in nonviscous solvents $\tau_{\theta 2} \approx 10^{-11}$–$10^{-10}$ s,[72] this is the reason for the requirement of very fast sublevel selective $T \rightarrow S_0$ transitions in a molecule or in a reactive intermediate to provide a nonequilibrium population of spin states in a system and to achieve MFE's in accordance with the triplet mechanism.

One can expect much larger MFE's in viscous solvents and frozen solutions, single crystals, and other media which restrict the rotation of a triplet and thus encourage the effect of anisotropic SOC-induced interconversion, which is the source of MFE according to TM. It should be noted in this connection that it was reported in the 1970s and in 1981 that the luminescence of certain organic molecules in glassy matrices and monocrystals at low temperature strongly depends upon an external magnetic field.[73-77] At that time the phenomenon was adequately interpreted within the framework of TM. However, only in the 1980s have the ideas developed in the course of photophysical research been applied to describe liquid-phase photochemical reactions.[59,60] An increase in the MFE with increasing solvent viscosity has been confirmed recently,[41] see Figure 5.

Unfortunately condition 10b does not hold in cases where we may expect a large MFE on the radical escape ($|A| > 10\%$). In general, ϵ (eq 10b) is not necessarily less than 1, and the theory of MFE due to the triplet mechanism, employing the stochastic Liouville equation (SLE),[72,78-80] has been worked out in refs 60 and 69. Numerical and approximate analytical solutions of the SLE, which have been obtained in ref 60, are in good agreement with the experimental field dependence of A upon B.[59,60]

The action of different mechanisms of MFEs in free-radical reactions can overlap with each other. The separation of their contributions to the observed effects is a serious problem. In 1974, Adrian[66a] suggested a clever experiment that could confirm the TM rather uniquely. The proposed experiment involves the photolysis of compounds with plane-polarized light. In such a case a narrow packet of oriented photoexcited molecules can be formed in a disordered medium. The TM predicts a strong dependence of magnetic effects on orientation of photoexcited molecules in an external magnetic field; thus, the polarized light-induced anisotropy of orientational distribution of molecules may result in the generation of an induced dichroism of magnetic effects even in isotropic media. The calculation[66] of initial polarization P of electrons of RP shows that this value varies as $P \approx 3\cos^2\chi - 1$ and is dependent on the angle χ between vectors **E** (electric field vector of excited light) and **B**. The result presented in ref 66 has been obtained within the model of isotropic triplet decay and is confined to the situation when the stochastic perturbation theory is valid.

The theoretical prediction[66] of the dependence of P upon χ has been tested in a few cases.[56,81-85] However,

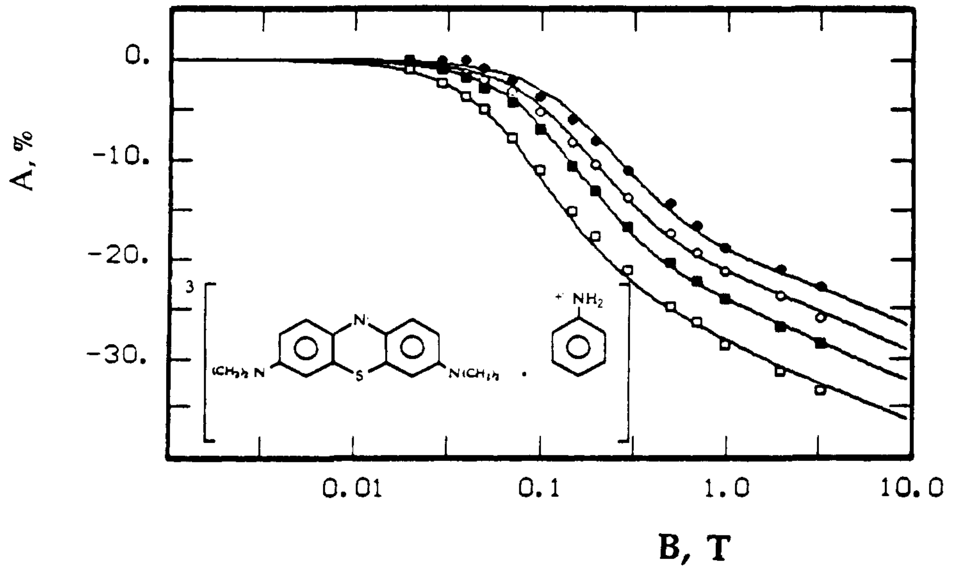


Figure 5. The dependences of MFE on a free-radical yield in photoelectron transfer between Methylene Blue in a triplet state and *p*-iodoaniline on magnetic flux density in solvents of different viscosities. Solvents were different binary mixtures of methanol and ethylene glycol; the higher the viscosity, the larger the |A|. Solid lines show theoretical results from combined triplet mechanism and Δg radical-pair mechanism (from ref 41).

in the careful study of CIDEP in the photoreduction of 1,2,4,5-tetracarboxylbenzene by triethylamine no significant deviation of $P_{\parallel}$ ($\chi = 0°$) from $P_{\perp}$ ($\chi = 90°$) has been observed.[56]

From theory, the polarization formed by the TM is maximal in the region of intermediate fields, namely $\omega_0 \approx D$, where D is the main fine structure parameter of the triplet state.[1,69] In this connection, the results of ref 68 are of interest; it has been shown that precisely in this situation (provided $D\tau_{\theta 2} \geq 1$), an inversion of the sign of the effect $\Delta P = P_{\parallel} - P_{\perp}$ occurs. Moreover, ΔP is close to zero even in the region of $D\tau_{\theta 2} \leq 1$.[68] Spin-selective decay of a triplet may also lead to the disappearance of any difference between $P_{\parallel}$ and $P_{\perp}$, if there is an equality of the population and deactivation rates for the T state and $k_d \approx |D_k| \approx \sum_i k_{T_iS}$.

The magnetophotoselection technique is well known in conventional ESR spectroscopy as a convenient experimental method, which allows one to simplify the analysis of ESR spectra of triplet molecules in glasses.[7] It has been used also in triplet energy transfer studies in solutions of viscous liquids. This method may find wide application in the studies of MFE's in radical reactions in viscous media. Theoretical predictions of the magnetophotoselective effect[66] have not been confirmed experimentally[56] (see above) probably due to a combination of factors.[68,71] It has been demonstrated that pumping the system with polarized light can lead to a dependence of triplet lifetime τ and, therefore MFE A, upon χ:

$$\tau \sim 3\cos^2\chi - 1 \qquad (15)$$

provided the triplet-state decay is an electron-spin-selective process.[71] It has also been shown that $\Delta A = A_{\perp}(\chi = 0°) - A_{\parallel}(\chi = 90°)$ in low-viscous solution cannot exceed 1% even at a very high magnetic flux density and with very fast S_1–T_1 transitions, see for details ref 71. At the same time one can expect much higher ΔP values and the anisotropy of the magnetic field effect (ΔA values) in media which hinder the rotation of triplet molecules.[68,71] Very recently the method of magnetophotoselection utilizing fast ESR spectroscopy was successfully used to study the decay of spin polarization of the triplet state of an expanded porphyrinoid, stable diprotonated form of sapphyrin dication in isotropic matrices.[86] It is possible that the observed magnetic effect anisotropy of the quantum yield of triplets formed by recombination of IRP's in quinone-depleted photosynthetic reaction centers (*R. spheroides*, R-26) suspended in very viscous media[87] can be explained by the TM.

The basic physical picture of the TM phenomena (spin selectivity of various reaction channels due to symmetry selection rules governed by SOC) is quite general and is also applicable to cases which involve reaction intermediates with $S > 1$. Actually, a MFE on the rate of CO rebinding to the ferrous ion in human hemoglobin after photolysis of the adduct below 20 K has been found in ref 88. As a result of the CO binding, the ferrous ion changes from a high-spin ($S = 2$) to a low-spin ($S = 0$) configuration. The process occurs via tunneling through a barrier, whereby SOC involving an excited intermediate state with $S = 1$ is believed to be involved.[88-90] The origin of MFE on this reaction arises through the field-induced mixing of the quintet ($S = 2$) zero-field substates and redistribution of the populations among the Zeeman sublevels.[90]

3.3. Δ*g* and "Hybrid" Mechanisms

It was mentioned already in section 2.3 that SOC causes the *g* factors of most radicals to differ from the free electron value, g_e, and to be anisotropic. The deviation of any one of the principal components (g_{xx}, g_{yy}, and g_{zz}) from g_e can be estimated for free radicals of hydrocarbons with nondegenerate ground state by the following approximate formula:[91]

$$g_{ii} - g_e = \sum_{A} \rho_A \xi_A / \Delta E_A \qquad (16)$$

where summation is over all the atoms A in the radical;

ρ_A is the spin density on atom A, ΔE_A is the energy difference between a singly occupied orbital and the next orbital of different symmetry closest in energy. The parameter ΔE_A finds analogy with parameter Δ discussed in the section 2, and formula 16 holds true under the condition $\xi_A \ll \Delta E_A$. Mixing of a singly occupied orbital with an orbital of lower energy will lead to the value of g_{ii} being larger than g_e, and mixing with an orbital of higher energy will lead to the value of g_{ii} being smaller than g_e.

The so-called "Δg mechanism" is another source of MFE's in free-radical reactions for which SOC is a critical interaction. The origin of the Δg mechanism is a difference of Larmor frequencies, resulting from different g factors, of the two spins in a correlated radical pair. As a result, an external magnetic field causes coherent transitions between the overall singlet (S) and triplet (T_0) spin states of a *spatially well-separated* geminate RP. It is less likely that the Δg mechanism will be operative for contact geminate pairs, because the operation of electron exchange in contact pairs will split the energy of S and T_0 to such an extent that the spin decoupling due to g-factor differences will be insufficient to offset the coupling of the electron spins due to the exchange interaction. According to the Δg mechanism, recombination or escape product yields depend on the combined action of periodic $T_0 \leftrightarrow S$ coherent spin motion and stochastic in-cage reencounters of the RPs. For a triplet precursor of the RP the sign of the MFE is always negative ($A < 0$), when the Δg mechanism is the only one operating.

Numerous examples of manifestations of the effect as well as the relevant theory are presented in refs 1–6. Usually for organic free radicals $\Delta g \sim 10^{-2}$–10^{-3}. In order to provide a mechanism that competes with the typical lifetime of spin-correlated RP's (ca. 10^{-8} s), the Δg mechanism for organic radical pairs may be effective only in strong fields ($B \geq 1$ T), where the frequency of $T_0 \leftrightarrow S$ transition given by

$$\omega_{T_0S} = \Delta g \beta_e B/(h/2\pi) \qquad (17)$$

may reach rather high values, i.e. 10^8–10^9 rad s^{-1}.[1,4] However, when the SOC energy in one of the radicals constituting a spin-correlated RP increases (for example, by heavy-atom substituents), the Δg value increases, and this channel of MFE origination shifts in the direction of low fields, cf. eq 17.

The effect of relatively low ($B \leq 0.2$ T) field on the yield of p-benzosemiquinone free radicals ($QH^\bullet$) obtained under photooxidation of hydroquinone with uranyl nitrate has been studied in viscous liquids ($\eta = 10^2$–10^3 cP).[92] It has been found that the application of an external magnetic field decreases the quantum yield of $QH^\bullet$. The $|A|$ value increases with an increase in the magnetic flux density and decreases with an increase of the presence of the magnetic isotope ^{235}U. The large difference between the g factor of $QH^\bullet$, which is practically isotropic ($g \sim 2.00$), and $\mathbf{g}$ tensor components of uranoyl (UO_2^+) free radical ($g_\parallel \approx 0$) leads to enormous values of $g(QH^\bullet) - g_\parallel(UO_2^+) \approx 2.0$, i.e., 100–1000 times higher than for typical organic radicals. In fact, under certain orientations of UO_2^+ in a magnetic field $\omega_{T_0S} = 10^{10}$ rad s^{-1} ($B = 0.2$ T) according to eq 17, and fast interconversion can occur in RP's possessing a large g-factor difference even with the application of a relatively weak magnetic field.[92] This fact may explain the absence of MFE in weak fields if the content of ^{235}U is more than 10%, because the increase in magnetic isotope content leads to an increase of effective hyperfine coupling (HFC) constant of RP, and the action of a HFC mechanism is opposite to that of the Δg mechanism.[92] Thus the rate of ISC according to a HFC mechanism in the RP under consideration is apparently the same as that of ISC induced by Δg mechanism even in low magnetic fields.

A huge difference of g factors of radicals forming spin-correlated RP explains a significant MFE value A $\approx -20\%$ ($B = 0.8$ T), which has been observed in the Fe^{3+}-catalyzed decomposition of hydrogen peroxide.[93] As a catalyst, the dimeric complex of Fe^{III}/EDTA was used; the difference of g factors of radicals in RP $[Fe^{3+},O_2^{\bullet-}]$ was about $\Delta g \sim 2.0$.[93] Further experiments,[94] however, did not confirm the results of ref 93.

A Δg-induced negative MFE has been observed in the photochemical formation of hydrated electrons during the photolysis of copper(I) cyanides. The large SOC value of Cu(II) complex is responsible for the large $\Delta g = 0.3$ in the geminate pair $[Cu^{2+},e^-_{aq}]$. As a result, MFE has been observed for this system even in relatively weak magnetic fields ($B \approx 2$ mT).[95]

Thus, strong SOC in one of the radicals constituting the spin-correlated RP can shift the action of a Δg mechanism to the region of weak magnetic fields ($B \sim 1$ mT), which are typically characteristic of the HFC mechanism of MFE. However, in the case of HFC-induced MFE, a variation of $|A|$ values for systems with variation of the nuclear isotope is expected as a definite mechanistic test.

An interesting example of the combined action of the triplet mechanism and the Δg mechanism has been established recently.[41] The MFE on free-radical yield e in the electron-transfer quenching of Methylene Blue by p-iodoaniline in homogeneous solutions of different viscosities was studied in ref 41. Figure 5 presents the experimental data and the results of a theoretical analysis of the MFE in a Methylene Blue photoreduction reaction based on the simultaneous action of TM and Δg mechanisms. It has been shown that the observed absence of a plateau region in A vs B dependence under high B ($B > 0.5$ T, Figure 5), where the contributions due to TM are expected to be saturated, can be nicely accounted for by the simultaneous action of the Δg mechanism in RP.

So, in a general case one can expect the simultaneous action of different mechanisms, and only a detailed analysis of the data (dependences on B, HFC, Δg as well as upon the position of heavy atoms in a systematic series of structures) will allow the identification of the different mechanisms and their relative contributions.

The basic qualitative idea about the role of coherent $S \leftrightarrow T_0$ transitions, induced by the difference of Larmor frequencies of the electrons constituting the spin-correlated pair, in radical reactions is quite general. The very similar mechanism of MFE's could be operative even in a case of isolated molecules in the gas phase, where rates of interconversion are affected by an external magnetic field.[96-99] It is clear, from general considerations, that intramolecular SOC creates different local magnetic fields at the positions of valence electrons localized on orbitally different MO's (see section 2.2.2). As a result, the precession frequencies of the two electrons in an external magnetic field might differ from each other. This qualitative picture of the phenomena was suggested and verified by semiempirical quantum chemical calculations in ref 97. It has been shown that, due to the action of SOC, the interaction of an external magnetic field with orbital angular momentum should mix states of different orbital symmetries and spin multiplicity ($\Delta S \neq 0$).[97-99] This may lead to MFE's on intramolecular radiationless transitions and thus to magnetokinetic effects in the gas phase, where RP-type mechanisms cannot operate.[4]

We have mentioned in section 2.4, that strong intraradical SOC may result in a mixing of S and T states of a "normal" geminate RP even in the absence of an external magnetic field. Under application of a magnetic field this could lead to a new mechanism of MFE's in radical reactions. This fact has been mentioned in ref 49 for the first time and has been termed a *hybrid mechanism*, because it encompasses the main features of the TM and the Δg mechanism. This mechanism has been applied in the interpretation of the observed field dependence of yields of radical ions obtained during photooxidation of $\mathrm{Ru(bpy)_3}^{2+}$ by *N,N'*-dimethyl viologen in aqueous solutions.[49] (We will discuss this reaction in more detail in sections 5.4.) According to refs 49 and 50, the hybrid mechanism can be a main source of magnetosensitivity for a wide class of photoreactions of transition metal complexes. Further theoretical and experimental research in this field is of paramount interest.

Rather strong MFE's on the quantum yield of photoaquation of $\mathrm{Rh(NH_3)_5X^{2+}}$, where X = $\mathrm{Cl^-}$, $\mathrm{Br^-}$ and of $\mathrm{Co(CN)_6{}^{3-}}$ (in the latter case $A \approx 100\%$) in pulsed magnetic fields up to 2.4 T have been found by Ferraudi et al.[100,101] It is interesting, that in the former case,[100] a magnetic field quenches the photoaquation of ammonia ($A < 0$) and enhances the photoaquation of the acido ligand ($A > 0$). Authors from the same group also studied the influence of strong magnetic fields (up to 9 T) on the rate of outer-sphere electron-transfer reactions between coordination complexes:[102]

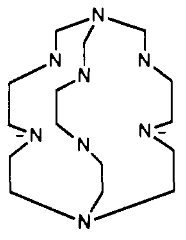
$$\mathrm{Co(NH_3)_6{}^{3+} + Ru(NH_3)_6{}^{2+} \rightarrow Co(NH_3)_6{}^{2+} + Ru(NH_3)_6{}^{3+}} \quad (18)$$

$$\mathrm{Co(NH_3)_6Cl^{2+} + Ru(NH_3)_6{}^{2+} \rightarrow Co(NH_3)_6Cl^{+} + Ru(NH_3)_6{}^{3+}} \quad (19)$$

$$\mathrm{Co(NH_3)_6{}^{3+} + Co(sep)^{2+} \rightarrow Co(NH_3)_6{}^{2+} + Co(sep)^{3+}} \quad (20)$$

$$\mathrm{Co(en)_3{}^{3+} + Co(sep)^{2+} \rightarrow Co(en)_3{}^{2+} + Co(sep)^{3+}} \quad (21)$$

Here "en" is ethylenediamine, and the structural formula of "sep" is as follows:



sep

It has been shown that the rate of electron transfer in reactions 18–21 exhibits a complex nonmonotonic dependence on the field.[102]

These observations were discussed in terms of magnetic field effected populations of Zeeman sublevels and the magnetic dipole mixing of the initial, or transition, state with other nearby states of appropriate symmetry.[100-104] It was assumed that RP mechanisms are not responsible for the observed MFE's.[100-104] At the same time the following basic concepts of the theory of the MFE such as the creation of MFE in RP's, as well as the role of SOC and spin–lattice relaxation within a complex, has not received detailed consideration yet.

4. *Spin–Orbit Coupling as a Quencher of Magnetic Field Effects*

4.1. Paramagnetic Relaxation Induced by Spin–Orbit Coupling

In section 3 we discussed the role of SOC as a source of MFE's. However, as will be demonstrated below, in molecular systems containing atoms heavier than fluorine, SOC simultaneously serves as an important interaction responsible for spin–lattice relaxation, which can destroy nonequilibrium populations produced by TM and which can also serve as a quencher of the Δg mechanism of intersystem crossing. This important feature of SOC can hinder the search for new magnetokinetic effects for compounds with heavy atom(s) and destroy or seriously reduce MFE's.

The theory of electronic spin–lattice relaxation (SLR) for systems with "quenched" orbital angular momentum (triplet organic molecules, transition metal complexes with nondegenerate orbital ground state, free polyatomic radicals) and weak SOC ($\Delta \gg \xi$, see section 2) is well developed and is presented in detail in many monographs (see, e.g. refs 33, 80, 105, and 106). Therefore, we restrict ourselves below to a brief analysis of the main theoretical concepts related to the problem of liquid-phase SOC-induced paramagnetic relaxation in $S = {}^1/_2$ systems with $L = 0$.

In order to describe electron spin lattice relaxation (in the following, unless specified, the term spin will refer to electronic spin) one has to find an acceptable answer to two fundamental questions: (i) what is the dominant interaction which creates the coupling between the spin subsystem and the bath? (ii) what is the main source of the stochastic modulation of the dominant interaction?

4.1.1. Magnetic Field Fluctuations

There are three important modes by which the spin subsystem interacts with the bath in free polyatomic radicals:

(i) anisotropic Zeeman interaction (external magnetic field)[1-6]

$$V_Z \approx \omega_0|\delta g| \le 10^{-2}\omega_0 \quad (22)$$

(ii) spin-rotational coupling (internal magnetic field)[107]

$$V_{SR} \approx 3\omega_r|g_s - g_e| \le 100\ \text{mT} \quad (23)$$

where ω_r is the average angular velocity of the free rotator.

(iii) anisotropic hyperfine interaction (internal magnetic field)[1-16]

$$V_{HFC} \approx |\delta A| \le 10\ \text{mT} \quad (24)$$

Here $g_s = (2g_\perp + g_\parallel)/3$ is the isotropic part of the **g** tensor, $\delta g = g_\perp - g_\parallel$ and $\delta A = A_\perp - A_\parallel$ describe the difference between the principal values of **g** tensor and tensor of hyperfine coupling **A**, respectively (if **g** and **A** have axial symmetry). Usually for organic radicals $\delta g \approx 10^{-3}$–10^{-2}. As a result, in relatively strong fields ($B \approx 1$ T) the anisotropic Zeeman interaction becomes larger than anisotropic HFC. It is important to note that in the cases i and ii undoubtedly SOC creates the fundamental coupling between the spin system and the bath, since it is responsible for the **g**-tensor anisotropy:[33,36]

$$\delta g \approx \xi/\Delta \quad (25)$$

and makes it deviate from the value of a free electron, g_e (see also section 2.3).

The same considerations hold true for transition metal complexes with effective spin $S = {}^1/_2$ and nondegenerate orbital ground state ($L = 0$), which can be considered as a special interesting case of polyatomic free radicals.

Stochastic molecular reorientations modulate anisotropic Zeeman and hyperfine interactions. For axially symmetric radicals this process leads to SLR with the rate:[33,80]

$$1/T_1(M_I) = 2/15(\omega_0\delta g/g_s - \delta A M_I)^2\tau_{\theta 2}[1 + \omega_0{}^2(M_I)\tau_{\theta 2}{}^2]^{-1} \quad (26)$$

where M_I is the corresponding nuclear magnetic quantum number.

Relaxation of rotational momentum of a radical leads to a random modulation of the spin-rotational interaction and the effectiveness of this modulation is related to the SOC of the system. As a result, one or more channel of SLR are opened by the occurrence of SOC. The relaxation time of rotational momentum τ_J for many-atom systems is very short in a nonviscous liquid ($\sim 10^{-13}$ s).[72] That is why even in strong magnetic fields ($B \approx 10$ T) the inequality $\omega_0\tau_J \ll 1$ will hold true, and the SLR induced by this process should not depend upon a flux density of an external magnetic field.[107,108] For systems with completely quenched orbital momentum (orbitally nondegenerate ground states, $L = 0$) and weak effective SOC, i.e. $\Delta \gg \xi$ (see section 2) the rate of SLR induced by stochastic modulation of spin-rotational interaction is given by[107,108]

$$1/T_1(\text{SR}) = 1/T_2(\text{SR}) = (2k_BT\sum_i(g_{ii} - g_e)^2\tau_J)/(3I) \quad (27)$$

Here I is the moment of inertia of a radical; g_{ii} are the main values of electron **g** tensor; $i = x, y$, and z; for axially symmetric radicals $g_{xx} = g_{yy} = g_\perp$, $g_{zz} = g_\parallel$.

In order to avoid the use of an additional parameter τ_J, one can refer to eq 28, relating τ_J with the readily measured (or calculated) value of $\tau_{\theta 2}$:[108]

$$\tau_{\theta 2}\tau_J = I/(6k_BT\gamma) \quad (28)$$

where γ is an empirical correction factor; when $\gamma = 1$ this is the well-known Hubbard relation.[72,108] Using eq 28 one can easily obtain the following formula for $1/T_1$(SR),[109] which is used for practical applications:

$$1/T_1(\text{SR}) = \sum_i(g_{ii} - g_s)^2/(9\tau_{\theta 2}\gamma) + (g_e - g_s)^2/(3\tau_{\theta 2}\gamma) \quad (29)$$

The overall rate of longitudinal SLR is given by

$$1/T_1 = 1/T_1(\text{SR}) + 1/T_1(M_I) \quad (30)$$

In a strong magnetic field ($\omega_0\tau_{\theta 2} \gg 1$) the ratio κ between rates of longitudinal relaxation induced by different mechanisms of SLR is the following:

$$\kappa = T_1(\text{SR})/T_1(M_I) = 0.3\gamma\delta g^2/\sum_i(g_{ii} - g_e)^2 \quad (31)$$

Equation 31 enables one to use the known parameters of the **g** tensor to determine which of the mechanisms makes the dominant contribution to the SLR process. This specified procedure has been suggested and realized for $\gamma = 1$ in ref 110. For a number of tetrahalogen-*p*-benzosemiquinone radical anions the parameter κ equals 0.17, 0.19, and 0.29 for the chloro-, bromo-, and iodo-substituted radicals, respectively.[110] That was the basis for the authors of ref 110 to come to the conclusion that, for the systems under consideration, the dominant contribution to longitudinal relaxation is made by spin-rotational interaction. The growth of SOC in a radical leads simultaneously to the increase of anisotropic Zeeman and spin-rotational interactions. The increase of a nuclear charge of a substituent usually leads to a dominant contribution of the anisotropic Zeeman interaction. However, T_1(SR) is always less than $T_1(g)$ for $\gamma = 1$!

It is important to note that the Hubbard relationship seems poor for charged particles in solvents with hydrogen bonds. In such solvents the parameter γ can exceed unity, and the relaxation due to modulation of anisotropic Zeeman interaction can be more effective than the spin-rotational relaxation.[109] In any case, in strong magnetic fields only this mechanism of longitudinal SLR can be expected to compete with the spin-rotational relaxation in liquids.

Due to the independence of the spin-rotational relaxation in the condensed phase on the external magnetic field, the increase of the rate of this process under an increase of SOC in free radicals can result in spin equilibration of a system and quenching of MFE's. However, this effect is expected to manifest itself only in media, strongly restricting translational motion of radicals (micelles, porous glasses, etc.),[4,5,111] because the typical rate of relaxation (for $S = {}^1/_2$ systems with $L = 0$ and weak SOC, $\Delta \gg \xi$) according to a spin-rotational mechanism $1/T_1$(SR) is low, namely $\sim 10^4$–10^6 s^{-1} [107,110] in nonviscous solutions.

According to Hayashi et al.,[111] SOC in heteroorganic radicals containing heavy atoms induces the relaxational transitions from T_+ and T_- sublevels and decrease MFE's in photogeneration of such radicals in comparison with photogeneration of carbon-centered radicals. Such an effect has also been considered in other publications.[112-114]

An interplay between MFE's of different SOC-dependent origins has been observed during photoreduction of triplet thionine by aniline and halogen-substituted anilines in micellar solutions.[112] It has been found that for most of the donors used, A > 0.[112] The positive MFE was saturated at fields of $B > 0.1$ T; this fact is usually ascribed to the result of joint action of HFC and relaxation mechanisms induced by anisotropic HFC.[115] However, the A value decreases with an increase in SOC in a sequence of donors—aniline, *p*-chloroianiline, *m*-bromoaniline, *o*-bromoaniline. This regularity has been tentatively explained by the increase of SRR contribution, whose rate is independent of an applied external magnetic field and increases with an increase in the radical's SOC.[112] In the case of *p*-iodoaniline, which possesses the maximum SOC within the series of donors used, not only does the positive MFE disappear but it even crosses over to negative values. This means that in this system the SRR completely inhibits the field dependence of spin evolution in a spatially well-separated RP, and the triplet mechanism (see section 3.2) gives the main contribution in the observed MFE.[112] However, recent experiments with reverse micelles[116-118] of variable size have provided clear evidence that the SOC-induced quenching of the MFE described in ref 112 is largely due to a SOC enhanced T → S interconversion from a contact triplet RP to the singlet diamagnetic products (see also section 4.3). It is quite possible that in systems under consideration in the region of relatively high fields ($B > 0.1$ T) simultaneous action of the mechanisms with opposite signs of A takes place: the SOC-induced TM (A < 0), which operates at the contact exciplex stage, and HFC mechanism (A > 0), which operates during intervals between reencounters and repeated contacts of radicals. We shall note that the role of HFC and relaxation mechanisms sharply increases in micellar solutions due to the increase of the effective lifetime of a geminate RP[119] and the enormous increase in the number of geminate reencounters.

The SLR process induced by magnetic dipolar interaction between electron spins of a RP in micelles has been first considered by Hayashi and Nagakura.[115] These authors used the following model: two spins are held at a fixed distance and their mutual orientation undergoes isotropic rotational diffusion. It is clear that this model corresponds to the case where the spins are fixed within a rotating triplet molecule. Consequently, the rate of longitudinal SLR is described in eq 13. However, a realistic model of the process should take into account the translational motion of radicals in the volume or on the surface of a micellar supercage. This fact was pointed out in ref 116, where a quantitative treatment of dipolar SLR in case of 3D and 2D translational diffusion has been done. It has been shown, that at fields $B > 10$ mT, the electron spin-dipolar relaxation may quantitatively account for the experimental data on the magnetic field dependent recombination kinetics of photochemically generated organic RP's in a reverse micellar medium.[120]

4.1.2. Electric Field Fluctuations

We shall discuss now another mechanism of SOC-induced spin-lattice relaxation not related to rotational or translational modulation of magnetic interactions. This mechanism was suggested by Kronig[121] and Van Vleck,[122] and it is well known in the ESR spectroscopy of transition metal complexes.[36,106] The physical basis of this mechanism is that the vibrations of atoms of a crystal lattice lead to a random modulation of the electric field in which the paramagnetic ion is embedded; this modulation leads to modulation of Δ and thus SOC. Modulation of SOC can induce electron-spin relaxation. In a liquid, thermal movement of solvent molecules perturbs the vibrations of a paramagnetic complex, the shape of a solvate shell and/or its contents. Consequently, the electric field of ligands and, therefore, SOC in a system are stochastically modulated. As a result fast paramagnetic relaxation may be induced.

The rate of SLR determined by the Kronig–Van Vleck mechanism increases with the strength of SOC and orbital–lattice coupling and decreases with the increase of crystal-field splitting. The functional dependences of the longitudinal relaxation between components of a Kramers doublet are described by formulae similar to eq 26:[123]

$$1/T_1 \approx \omega_0^{\,2}(\xi/\Delta)^2 a^2 \tau_c/(1 + \omega_0^{\,2}\tau_c^{\,2}) \qquad (32)$$

This is the Van Vleck one-phonon process, and eq 33 holds true for

$$1/T_1 \approx (\xi/\Delta)^2 a^4 \tau_c^{-1} \qquad (33)$$

the Van Vleck two-phonon or Raman process. In eqs 32 and 33 the parameter $a^2 = (\phi/\Delta)^2 \times 10^{-2}$, where the electric field potential ϕ indicates the appropriate magnitude of solute–solvent (orbital–lattice) interaction. The correlation time of the process, τ_c, plays the same role here as $\tau_{\theta 2}$ in eq 26, and is a characteristic time of the fastest modulation process of the electric field potential around the paramagnetic ion. In the liquid phase it could be, for example, the dissipative transfer of vibrational energy into a thermal motion of its nearest neighbors,[106] or the process of collisional modulation of the solvate shell of an ion.[124-126] In both of these cases $\tau_c \approx 10^{-12}$ s.

Another important mechanism of SLR, which is also related to the fluctuations of electric field potential ϕ, was proposed by Orbach.[127] This mechanism is very similar to the Kronig–Van Vleck mechanism, except that the spin flip is accompanied by a simultaneous transition into an excited electronic state. The Orbach process in liquid solutions and systems with $S = {}^1/_2$ leads to the following estimation of the SLR rate:[123]

$$1/T_1 \sim (\xi/\Delta)^2 a^2 \tau_c^{-1}/[\exp(\Delta/k_B T) - 1] \qquad (34)$$

For systems with orbitally nondegenerate ground states ($L = 0$) this process could be the most effective mechanism of SLR if a low-lying excited electronic level is present ($\Delta \leq 5\,k_B T$). If no such low-energy excited state exists, the Orbach mechanism becomes negligible.

Indirect measurements of electron paramagnetic relaxation in liquid solutions by NMR show that $1/T_1$ varies within a wide range, viz. 10^8–10^{11} s^{-1}, being dependent upon the structure of complex, spin-

Table III. Functional Dependences of Relaxation Rates $1/T_1$ for Different Mechanisms of SLR in Systems with $S = {}^1/_2$ with Completely Quenched Orbital Momentum ($L = 0$; $\Delta \gg \xi$)

interaction	modulation by	correlation time, s	expression for $1/T_1$
anisotropic Zeeman (external magnetic field)	stochastic jumps in the angular space	$\tau_{\theta 2} \approx 10^{-11}$–$10^{-9}$	$\sim(\xi/\Delta)^2\omega_0^2\tau_{\theta 2}/[1 + \omega_0^2\tau_{\theta 2}^2]$
spin-rotational (internal magnetic field)	stochastic molecular rotations in a condensed media	$\tau_J \approx 10^{-13}$	$\sim(\xi/\Delta)^2 k_B T\tau_J/I = (\xi/\Delta)^2\tau_{\theta 2}^{-1}$
electric (Coulomb field of nearest neighbors)	stochastic vibrations and/or collisions	$\tau_c \approx 10^{-12}$	$\sim(\xi/\Delta)^2(a^2/\tau_c)\begin{cases}\times a^2, \text{ Van Vleck–Raman process}^a \\ \times[e^{\Delta/k_B T} - 1]^{-1}, \text{ Orbach process}\end{cases}$

[a] Here $a^2 = (\phi/\Delta)^2 \times 10^{-2}$; see text.

multiplicity and nuclear charge of the central ion.[106,124-126,128,129] A short correlation time τ_c leads to a dependence upon the external magnetic field only in the region of very strong fields ($B > 1$ T), for which the condition $(\omega_0\tau_c)^2 \geq 1$ holds.

The Kronig–Van Vleck–Orbach theory of SLR is proved for paramagnetic ions in low-temperature solid phase.[36,106] At the same time one may expect that this mechanism makes the dominant contribution to the SLR process also in liquid solutions of transition metal complexes[106,123] and other systems possessing relatively strong SOC. In fact, a viscosity-independent contribution to SLR of the triplet exciplex between Methylene Blue and *p*-iodoaniline has been found recently.[41] This observation was explained as a result of stochastic perturbations associated with the fast conformational changes of the exciplex.[41]

However one cannot expect relaxation rates larger than 10^9 s^{-1} according to the Kronig–Van Vleck–Orbach theory, for systems with $S = {}^1/_2$. This is the case even when the Orbach mechanism of SLR acts for systems with $\Delta \leq 5\, k_B T$, cf. eq 34 and Table III.

It is possible to draw the following conclusions from the above discussion. For systems with $S = {}^1/_2$ and completely quenched orbital momentum both stochastic modulations of magnetic interactions and fluctuations of electric field lead to the following dependence of the rate of SLR on spin-orbit coupling:

$$1/T_1 \sim (\xi/\Delta)^2 \tag{35}$$

provided SOC is small, i.e.

$$(\xi/\Delta)^2 \ll 1 \tag{36}$$

The origin of this functional dependence lies in the fact that in systems with $S = {}^1/_2$ and an orbitally nondegenerate ground state ($L = 0$), the SOC-induced SLR can be generated only by off-diagonal elements of the orbital momentum operator between electronic terms widely separated in energy.

The straightforward application of the functional dependence (eq 35) to systems with degenerate orbital ground states and large SOC $\xi \sim 10^2$–10^3 cm^{-1} would be generally expected to lead to very fast SLR. The latter expectation is probably the basis for the pessimism concerning the possible observation of MFE for systems possessing strong SOC. However, such a general conclusion may not be correct because, for systems with $\xi \approx \Delta$ (many transition metal complexes and linear inorganic free radicals) or with $\xi > \Delta$ (atomic radicals in solution), eq 35 may not be applicable.[130] We do not discuss here the problem of paramagnetic relaxation for which eq 35 becomes inapplicable, but a study of this problem is now in progress.[130]

The existence of both factors, strong SOC caused by heavy atom and closely spaced orbital states ($L \neq 0$) in a free radical, should lead to a fast paramagnetic relaxation resulting in an extreme broadening of ESR spectra of such a species. For example, no ESR signals of halogen atoms and of radicals with axial symmetry, such as hydroxyl $^\bullet$OH, alkoxy RO$^\bullet$, and alkylthio RS$^\bullet$, have been observed in the liquid phase. The ESR spectrum of $Ru(bpy)_3^{3+}$ ($3d^5$) was observed only at liquid nitrogen temperature (77 K)[39] and the ESR spectrum of NpO_2^{2+} ($5f^1$) only at liquid helium temperature (4.2 K).[131] At the same time ESR spectra of UO_2^+ ($5f^1$) species were observed at low temperature (153 K)[40] and even at room temperature.[132] Before any general conclusion can be made, further theoretical analysis of the paramagnetic relaxation in metal-centered free radicals is required as well as systematization of available experimental data.

At the same time, many spin effects and MFE's have been observed in reactions involving free radicals centered on heavy atoms, see section 5 below. Such MFEs reflect the existence of magnetosensitive coherent transitions in these systems. Thus, the presence of a heavy atom does not in itself provide a guarantee of the absence of MFE.

The important role of the unquenched orbital momentum in electron transfer reactions between triplet molecules and inorganic ions has been demonstrated experimentally[38,47,48] and will be discussed in more detail in section 5. It has been shown that the quantum yield of free-radical formation crucially depends on the value of the SOC energy and the degree of orbital degeneracy of the ground electronic state in the primary electron transfer products, namely inorganic free radicals.[38,47,48]

It was already mentioned in section 2.3 that the relaxation of the projection of electron angular momentum **J** in an atom along the internuclear axis of the atomic pair leads to transitions between the electronic states in a spatially well-separated geminate pair of atomic radicals. Therefore this process essentially affects the kinetics of recombination of atoms.

Thus the problem of electronic angular momentum relaxation in a condensed phase for Kramers systems with strong SOC and unquenched orbital momentum ($L \neq 0$) is not only of theoretical interest. Certainly under conditions of very strong SOC, i.e. when eqs 35 and 36 do not hold true, one can expect the existence of relaxation of other types, see ref 130 and references cited therein. There is a very limited number of publications devoted to this problem. In particular, Sceats[43] adopted the gas-phase model of collision-induced reorientation of electronic angular momentum

$J = {}^{3}/_{2}$,[133] for calculation of the rate of transitions between the electronic terms of geminate RP in the liquid phase recombination of iodine atoms.

A dilute liquid solution of atomic radicals is the simplest system which demonstrates the basic characteristics of **J** relaxation in systems with orbitally degenerate ground states and strong SOC. In a liquid, contrary to a gas, the interaction of a particle with the medium cannot be represented by a sum of binary collisions. All nearest neighbors of a particle or a primary solvent cage create an (anisotropic) electric field potential (like in the case of transition metal complexes ligands create the "ligand filed"), and the particle exists in such a potential. Therefore it is not clear to what extent the gas-like collisional model used in ref 43 can be used to model the real situation in a liquid.

At present the adequate description of electronic angular momentum relaxation for systems with strong SOC ($\xi \approx \Delta$) in a condensed phase is a challenge for theory.[130]

4.1.3. Relaxation Induced by External Heavy Atoms

The external heavy atom (EHA) effect is well known in photochemistry[7,10,32] and manifests itself in MFEs also. It has been mentioned already that the δg value is strongly dependent upon the SOC energy in a free radical, see eq 25. That is why it is possible to expect that even a small variation of SOC value can influence the rate of SLR. The enhancement of SOC in the collisional complex of a molecule and external heavy atom (EHA) leads to the well-known effect in photochemistry, i.e., to an increase of the rate of S–T transitions.[7,9,10,21] It seems obvious that an increase in SOC should also take place in the collisional complex [free radical, EHA]. Therefore, one can expect variations of principal values of **g** tensor and orientation of its axes in space. Quantum mechanical calculations of certain model systems, such as complexes of the $H_2{}^{\bullet}COH$ radical with halides (Cl^-, Br^-) confirmed this prediction.[134] Modulation of SOC, and thus the **g** tensor in the pair [organic radical, EHA] by molecular motion of the partners can result in the wandering of main axes of **g** tensor in the angular space even in frozen solutions.[134]

Observation of a EHA effect may be expected provided the following condition is met: the frequency of encounters of a free radical with EHA, Z_{en}, has to be higher or at least comparable to the frequency of free-radical reorientation, $\tau_{\theta 2}^{-1}$. In this case, the effectiveness of this additional channel of SLR strongly depends upon the concentration of the EHA and upon its nuclear charge.[134] The predictions of theory[134] have been confirmed in the course of study of EHA effect on the shape of ESR lines of certain free radicals in liquid solutions.[135] It has been found that the line width of an ESR spectrum of fluorescein semiquinone free radical in the presence of cesium chloride (0.15 M) is larger than that in the presence of sodium chloride at the same concentration. It has been concluded that this difference is not caused by different solvating properties of Cs^+ and Na^+.[135] One expects that the phenomenon can be found as well in other systems where the frequency of encounters between reagent and heavy atom is such that $Z_{en} \gtrsim \tau_{\theta 2}^{-1}$.[134,135]

Acceleration of a SLR process in the radicals constituting the geminate pair may become very effective when certain chemically inert paramagnetic species are added to the solution. There have been several reports of MFE's quenched by paramagnetic metal ions.[136-143] The effect is related to an exchange and/or magnetic dipole interaction between particles. As a result of very strong SOC in trivalent lanthanide ions, only a projection of the total electron spin onto the direction of total angular momentum, **J**, could serve as a measure of efficiency for the spin exchange process.[141] An interesting comparison of the quenching ability of 3d transition metal and 4f lanthanoid ions was made very recently by Sakaguchi and Hayashi.[144] It has been shown that the enhancement of SLR rate (MFEs quenching) by 3d ions is much larger than that of 4f ions. In contrast the quenching abilities of 3d transition metal ions (Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) are almost the same.[144] In general the quenching of MFE's by paramagnetic ions occurs according to different physical mechanisms, and their detailed description remains a challenge to theory.

A zinc porphyrin viologen dyad, when subjected to photoexcitation, forms a chemically-bonded triplet ion-radical pair (IRP).[145] The dyad has been solubilized in different micelles and the external magnetic field effect on IRP decay kinetics has been studied. A formal kinetics analysis of the data (see section 4.3 below) shows that at high field ($B = 0.24$ T) rate constant of IRP decay k_{obs} corresponds to k_{SOC}.[145] The rate constants $k_{obs} = k_{SOC} \approx 4.6 \times 10^5$ and 1.1×10^6 s^{-1} have been obtained for micelles of cetyltrimethylammonium chloride and cetyltrimethylammonium bromide, respectively. The increase of k_{SOC} in bromide ion-containing micelles has been connected with the SOC increase due to EHA effect.[145]

Inorganic salts containing heavy atoms (CsCl, NaBr, or NaI) dissolved in viscous solutions containing xanthene dyes, which undergo photoreduction, lead to a decrease of the magnetic field effect, A, in comparison with A for solutions containing NaCl at the same concentration.[135]

Upon the introduction of EHA's into micelles one can achieve relatively high local concentrations. This manifests itself in MFE's quenching,[146] and a formal kinetic analysis requires the inclusion of k_{SOC}.[146,147] For example, the dissolution of iodobenzene in sodium dodecyl sulfate (SDS) micellar solutions of benzophenone (acceptor) and *p*-phenylaniline (donor) up to a concentration of 10 iodobenzene molecules per micelle produces a 4–8-fold increase in k_{SOC}.[146] (At the same time it is necessary to recognize that the microenvironment of a RP in a micelle will be changed by heavily loading the micelle with an organic compound[148])

4.2. Weak CIDNP in Photoinduced Reactions of Compounds with Heavy Atoms

It is known that chemically-induced nuclear polarization (CIDNP) experiments can exhibit very high sensitivity.[1,149] NMR line-enhancement factors (V)[62] reflect spin correlation in spatially-separated RP's, and they are related to a number of parameters, in particular, the nuclear spin relaxation times in the radicals $T_{1n}{}^{R}$, electron spin relaxation times $T_{1,2}$, as well as the nuclear spin relaxation times T_{1n} in the diamagnetic products,

Scheme I

$$^3[R_1^\bullet, R_2^\bullet] \overset{HFC}{\rightleftharpoons} {}^1[R_1^\bullet, R_2^\bullet] \quad \text{ISC dependent upon nuclear spin}$$

$$^3[R_1^\bullet, R_2^\bullet] \overset{SOC}{\rightleftharpoons} {}^1[R_1^\bullet, R_2^\bullet] \quad \text{ISC independent of nuclear spin}$$

the difference (Δg) between g factors of radicals, and the hyperfine coupling constants A. The contribution of the contact RP to the creation of CIDNP is usually neglected.[150] Difficulties in interpretation and observation of CIDNP produced in reactions involving metal-centered radicals arise mainly due to the fact that $T_{1,2}$'s are usually shorter than those for C-centered free radicals.[129]

For observation of CIDNP as well as magnetic isotope effects (MIE) in a reaction proceeding via RP $[R_1^\bullet, R_2^\bullet]$ (or biradical) formation, it is necessary that the HFC mechanism[151] makes a significant contribution to the ISC process in the pair, see Scheme I. It is clear that SOC-induced paramagnetic relaxation of the radicals constituting the RP (see section 4.1) creates a nuclear spin-independent leakage of spin coherency, see Scheme I. Such an effect will lead to the reduction or complete destruction of the CIDNP effect. It was suggested also that SOC can open the nuclear spin-independent channel of direct recombination of contact triplet RP's to singlet products.[34,113,118] SOC also can serve as an interaction responsible for MFE's as was shown in section 3. All these factors lead to a decrease in the role HFC plays in the process of intersystem crossing and thus to a decrease of CIDNP and MFE's which proceed through the HFC mechanism. Again, such general considerations lead to a pessimism concerning the possible observation of CIDNP in systems involving radicals pairs for which one of the fragments possesses strong SOC.

In spite of this bleak outlook, we present below several examples of photoinduced ^{1}H CIDNP observed for organic compounds with heavy atom substituents and one comparative result on inorganic heavy metal compounds.

^{1}H CIDNP in the photoreaction of benzophenone (BP) as well as p-bromobenzophenone with hydrogen (electron) donors ($\mathcal{D}$H) such as phenol, aniline, their derivatives and in particular p-bromo-substituted derivatives have been well studied.[153] Photoreaction proceeds with the formation of a triplet RP, which dissociates or (after intersystem crossing) recombines with the regeneration of the starting reagents, which possess polarized nuclear spin populations:

$$^3(Br)BP + \mathcal{D}H \longrightarrow {}^3[(Br)BPH^\bullet, \mathcal{D}^\bullet] \qquad (37)$$

(formation of pair)

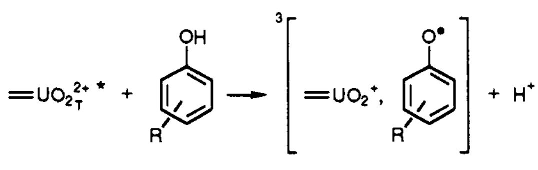
$$^3[(Br)BPH^\bullet, \mathcal{D}^\bullet] \nearrow (Br)BPH^\bullet + \mathcal{D}^\bullet \qquad (38)$$

$$^3[(Br)BPH^\bullet, \mathcal{D}^\bullet] \searrow {}^\dagger(Br)BP + {}^\dagger\mathcal{D}H \qquad (39)$$

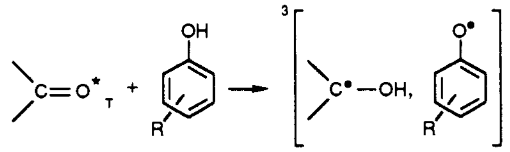
The sign † here and below denotes formation of products possessing nuclear polarization. The main observation of this study is that for bromo-substituted compounds the measured values of $|V|$ in most cases are lower than for the corresponding unsubstituted compounds.[153]

The ^{1}H CIDNP spectrum of photoexcited p-bromo dibenzyl ketone is very weak compared to that of dibenzyl ketone,[154] consistent with SOC-induced relaxation that competes with HFC-induced creation of nuclear polarization.

The photooxidation of phenols by uranyl salts in methanol results in the formation of ^{1}H CIDNP of starting phenols.[155] The photoexcited uranyl has been described as a nominal triplet state,[156] and the photooxidation reactions by uranyl possess a close and interesting analogy to the photochemistry of triplet benzophenone:[155,156]



(40)



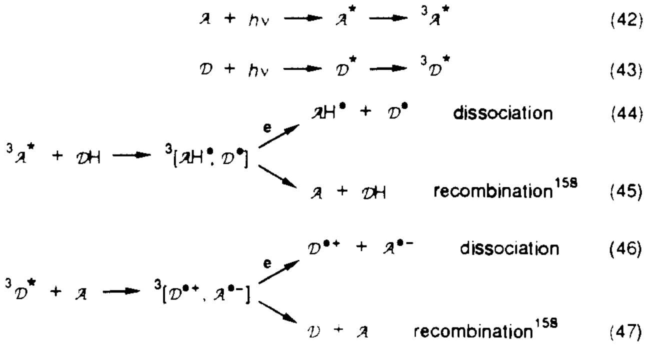
(41)

The rate-determining step of both reactions is supposed to be an electron transfer.[156,157] Photoxidation of phenols by these acceptors proceeds free radicals formation.[155-157] The observed enhancement factors $|V|$ of the NMR lines produced by reaction 40 were much lower than in the case of benzophenone photoreduction reaction 41. Thus, it appears that SOC-induced leakage of spin coherency can be responsible for the reduction of the CIDNP signal in the case of reaction 40.

The experimental data presented above cannot be considered as conclusive experimental evidence for mechanisms in which the relaxation rates, $1/T_{1n}{}^R$ and/or $1/T_{1,2}$, for radicals with heavy atoms are greater than for radicals which do not possess heavy atoms. It is known[1] that V values depend upon other radical parameters, in particular, difference of their g factors, which varies when radicals are substituted with a heavy atom. We believe, however, that the above data indicate the necessity to take into account contact RP's (see section 2.3) containing radicals with heavy atoms. Spin correlation in these RP's is expected to be lost more rapidly due to the SOC-induced fast T → S interconversion processes which wash out contributions of HFC and manifest themselves in the reduction of nuclear polarization. Having said this, we should also recognize that even with *very* heavy atoms, such as U in $UO_2{}^{2+}$, the SOC introduced by the heavy atom is not always sufficient to completely quench the observed CIDNP.

4.3. Photochemical Reactions of Compounds with Heavy Atoms

The presence of the SOC effect due to the presence of a heavy atom in a reactive molecule often reveals itself in photochemical reactions leading to the formation of free radicals. It is not surprising that most of these reactions are those of triplet molecules, because SOC associated with the heavy atom can increase the intersystem crossing yield.[7,10,12,13,32] We shall consider the heavy atom effect on photooxidation–photoreduction reactions of molecules in a triplet state ($^3\mathcal{A}$*, acceptor; ${}^3\mathcal{D}^*$, donor). The essence of the process reflects the following reaction scheme previously used in section 4.2:



$$\mathcal{A} + h\nu \longrightarrow \mathcal{A}^* \longrightarrow {}^3\mathcal{A}^* \qquad (42)$$

$$\mathcal{D} + h\nu \longrightarrow \mathcal{D}^* \longrightarrow {}^3\mathcal{D}^* \qquad (43)$$

$${}^3\mathcal{A}^* + \mathcal{D}H \longrightarrow {}^3[\mathcal{A}H^\bullet, \mathcal{D}^\bullet] \xrightarrow{e} \mathcal{A}H^\bullet + \mathcal{D}^\bullet \quad \text{dissociation} \qquad (44)$$

$${}^3[\mathcal{A}H^\bullet, \mathcal{D}^\bullet] \longrightarrow \mathcal{A} + \mathcal{D}H \quad \text{recombination}^{158} \qquad (45)$$

$${}^3\mathcal{D}^* + \mathcal{A} \longrightarrow {}^3[\mathcal{D}^{\bullet+}, \mathcal{A}^{\bullet-}] \xrightarrow{e} \mathcal{D}^{\bullet+} + \mathcal{A}^{\bullet-} \quad \text{dissociation} \qquad (46)$$

$${}^3[\mathcal{D}^{\bullet+}, \mathcal{A}^{\bullet-}] \longrightarrow \mathcal{D} + \mathcal{A} \quad \text{recombination}^{158} \qquad (47)$$

Reactions 42–47 are the generic representations of most of the photochemical redox reactions occurring via the triplet state that we will be referring to in this paper.[159] **e** refers to reactions leading to cage escape.

During the photoreduction of benzophenone and 7,8-benzoquinoline by phenol in nonviscous solvents, the radical-pair escape yield, **e**, equals unity as is expected for a triplet radical pair.[160,161] In fact, the lifetime of the RP in nonviscous solvent is so short, that even S–T evolution according to the HFC mechanism does not have enough time to occur, and the pair dissociates into free radicals with high efficiency. However, with halogen substituted phenols as reductants, **e** becomes less than unity.[160,161] The **e** values for 7,8-benzoquinoline photoreduction decrease for the following series: *m*-bromophenol (0.88), *o*-bromophenol (0.72), *p*-bromophenol (0.60), *p*-iodophenol (0.25).[161] (The corresponding **e** values are presented in parentheses.) It has been already mentioned above that provided all other conditions are comparable, the heavy atom effect manifests itself most effectively when the heavy atom is positioned at a place where the spin density is higher. The trend of the **e** values above confirms this principle, i.e., for 7π-electron aromatic free radicals (benzyl and radicals with heteroatom of generic formula $C_6H_5X^\bullet$) spin densities $\rho_{para} > \rho_{ortho} > \rho_{meta}$.[33]

A similar effect has been observed for triplet thionine photoreduction by halogen-substituted anilines in methanol.[60,162] It has been found that **e** equals 0.51, 0.45, 0.225, and 0.135 for *p*-bromoaniline, *m*-iodoaniline, *o*-iodoaniline, and *p*-iodoaniline, respectively.[60]

In electron transfer to triplet acriflavine from halogen-substituted anilines in acetonitrile, **e** equals 0.82, 0.78, 0.70, and 0.49 for aniline, *p*-chloro-, *p*-bromo-, and *p*-iodoaniline, respectively.[163,164] Clearly, **e** decreases as the nuclear charge of the halogen substituent increases.

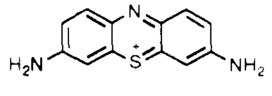
The heavy atom effect also manifests itself in the pattern of **e** values observed for electron-transfer reactions from ascorbic acid and cyanide metal complexes to photoexcited triplet xanthene dyes (${}^3\mathcal{A}^*$).[165] The experimentally measured values of **e** increase in the following sequence: fluorescein (HD) > eosine (bromo-substituted fluorescein, BrD) > eritrosine (iodo-substituted fluorescein, ID). In the quenching of ${}^3\mathcal{A}^*$ by complexes of Mo(IV) and that of W(IV), the value of **e** is lower than in quenching by ascorbic acid, but it is also decreases within the sequence HD < BrD < Rose Bengal. (The latter is iodo- and chloro-substituted fluorescein, which we will denote as ICID).[165]

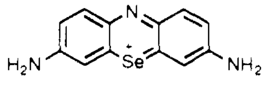
A strong influence of SOC on cage escape values was observed for the photooxidation of triplet molecules ${}^3\mathcal{D}^*$ by acceptor ($\mathcal{A}$) *N,N'*-dimethyl viologen (MV^{2+}).[166] The radical pair ${}^3[\mathcal{D}^{\bullet+}, MV^+]$ is formed in a reaction like eq 46. (The photooxidation of $Ru(bpy)_3{}^{2+}$ by MV^{2+} will be considered in section 5.4.) Reactions leading to the formation of such RP's induced by visible light are under intensive investigation in connection with solar energy storage.[166-168] The important problem here is to obtain a high yield of products, i.e., high **e**, and to avoid the reverse electron transfer as long as possible. When the donor $\mathcal{D}$ does not have heavy atoms $\mathcal{D}$ = 9-methylanthracene or Acridine Yellow), **e** $\approx$ 1.0.[166] In the case of 9-bromoanthracene **e** decreases to 0.74. When $\mathcal{D}$ is an osmium or ruthenium complex (in particular $Ru(bpy)_3{}^{2+}$), which forms metal-centered free radicals, **e** is rather small, viz. 0.14–0.27. An EHA effect was found also. It is found that in the photoreduction reaction of $\mathcal{D}$ = 9-bromoanthracene in a solvent mixture containing methyliodide, **e** decreases by more than a factor of 2 and falls to 0.3.[166]

The heavy atom effect manifests itself also in the decrease of the MFE on the yield of radicals which escape from a cage of a viscous solvent or from a micelle. (MFE is defined according to eq 9. If only HFC and relaxation mechanisms operate for triplet pairs: $0 < A < \infty$). The heavy atom effect on the MFE was studied in the photoreduction of a family of xanthene dyes, i.e. HD, BrD, ICID by *p*-cresol in water–glycerol media.[135] (The abbreviations of dyes are explained above.) The triad HD–BrD–ID is a classical example of the internal heavy atom effect in photochemistry: quantum yields of triplet state formation are 0.05, 0.71, and 1.05, respectively.[9] It has been found that for photoreduction A (±5%) equals 120% (HD) and 55% (BrD, ID, ICID), cf. Figure 6.[135] So, the tendency of A to decrease with an increase in nuclear charge *Z* of the halogen substituent is observed.[135]

The results of ref 153 on ${}^1H$ CIDNP in the photoreduction of benzophenone by aromatic compounds including bromo-substituted benzophenones have been discussed in section 4.1. MFE on radical yield for the same systems in viscous and micellar solutions was measured,[113,114,146,153,157] see eqs 37–39. The A values decrease upon the introduction of a heavy atom into one or both reagents' structure. In solutions whose viscosity ($\eta \approx 10^3$ cP) is much higher than the effective viscosity of micelles, the influence of the heavy atom is more pronounced.[114,153]

The MFE on the rate of geminate recombination of triplet RP's formed in water-in-oil microemulsions in the photoreduction of thionine by aniline and selenine, where a S atom is substituted by a heavier Se atom (see structures), was studied.[118] A decrease in MFE caused by internal heavy atom substitution was observed and it was ascribed to the SOC induced direct recombination of triplet RP into singlet products.[113,118] In other words, according to refs 113 and 118, reactions 45 and 47 can be single-stage SOC-induced processes without pre-





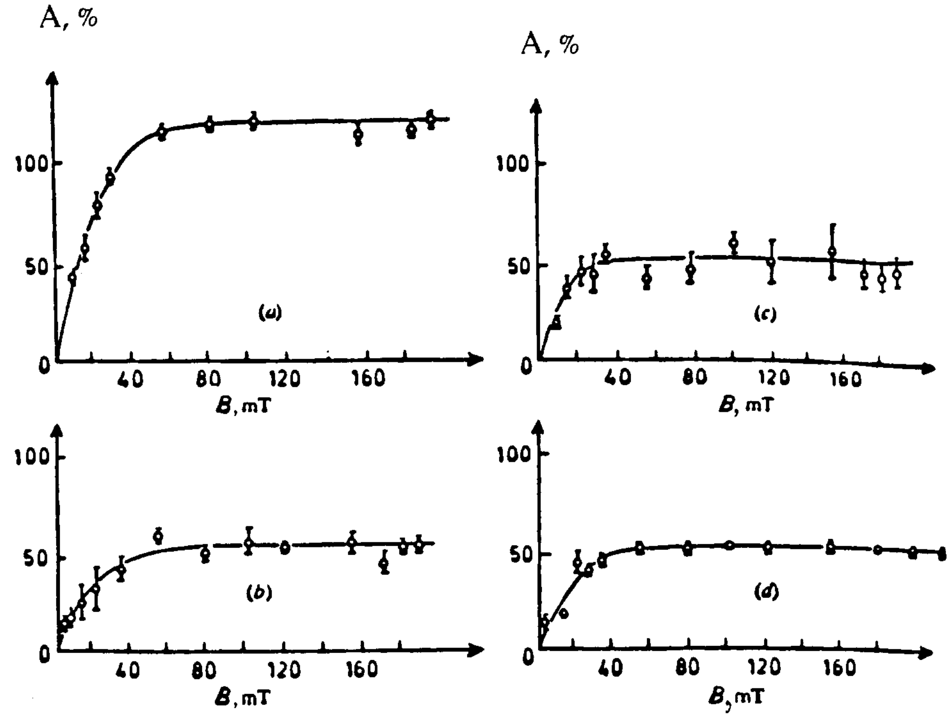


Figure 6. Dependences of MFE on the free radical yield in photoreduction of four xanthene dyes in a triplet state on magnetic field flux in the glycerol–*p*-cresol–ethanol triple mixture (89:10:1 v/v) at 295 K: (a) HD, (b) ID, (c) BrD, (d) ICID (from ref 135b,c).

liminary interconversion of a triplet into a singlet RP. Although such a possibility exists, it is not clear what exact distinction is meant between the "direct" formation of product and the process which involves a singlet radical pair. There is a limited set of relative orientations in which the pair may undergo an efficient intersystem crossing. It is possible, but not obvious, that electron transfer ("recombination") occurs from exactly the same set of orientations. It would seem, therefore, that the "direct" recombination mechanism from a triplet pair implies that the same orientations which promote intersystem crossing also promote electron transfer, and that the latter is faster, i.e., not rate limiting.

Data on MFE's in reactions of formation of heteroatom and metal-centered free radicals are of special interest. The SOC of atoms heavier than fluorine ($Z = 9$) is expected to enhance the leakage of spin coherency from geminate RP's containing such non-carbon-centered radicals and thus to decrease MFE's.[111] We shall consider below some pertinent experimental data.

MFE's in photoreactions of trialkylgermanes were studied in refs 169 and 170. During photooxidation of triethylgermane in micelles of SDS by the triplet acetophenone or xanthone, the RP ${}^3[{>}C^{\bullet}{-}OH,(C_2H_5)_3Ge^{\bullet}]$ is generated.[170] The study of the effect of a magnetic field (B = 1 T) on the ketyl radical yield revealed a MFE of A = 3 and 27% for acetophenone and xanthone, respectively.[170] It is worthwhile to mention, for the sake of comparison, that a majority of A values measured for photooxidation of different donors in SDS micelles by triplet carbonyl compounds is much higher, up to 60–260%.[153,171,172] The MFE A = 16 ± 2% (B = 1.35 T) was found for photolysis of methyltriphenylgermane occurring via a triplet RP with Ge-centered radical formation.[169] So, MFE's, in experiments with Ge-centered free radicals, are relatively small, but they do exist and they instill hope for the existence of a magnetic isotope effect (MIE) for heavy isotopes, in particular germanium.[170]

A MFE on the radical yield has not been found in a number of reactions where triplet RP's of the type ${}^3[UO_2^{\bullet+},R^{\bullet}]$ are formed.[156] At the same time, the effective HFC constants of these RPs are relatively small; it has been mentioned above that an indirect manifestation of HFC mechanism in these reactions has been reported in ref 92. Only one case exists to our knowledge, i.e., the study of MFE on rate of a polymerization reaction photoinduced by uranyl acetate,[156] where the MFE due to the HFC mechanism has been found for a RP of the type ${}^3[UO_2^{\bullet+},R^{\bullet}]$.

It is surprising that no MFE has been found for the photoreduction of benzophenone by thiophenol in SDS micelles ($B \leq 0.32$ T):[173]

$$ {}^3Ph_2CO^* + PhSH \rightarrow {}^3[Ph_2C^{\bullet}OH,PhS^{\bullet}] \qquad (48) $$

It was suggested that the reason for the absence of a MFE is a fast spin rotational relaxation rate (see eq 29) with $1/T_{1,2}(SR) \approx 5 \times 10^8\ s^{-1}$. However, a rather short $\tau_{\theta 2} \sim 10^{-13}$ s was substituted into eq 29 in order to obtain fast relaxation.[173] For organic radicals in SDS micelles, values of $\tau_{\theta 2} \approx 10^{-10}$–$10^{-11}$ s were determined experimentally.[174] Thus, the reason for the absence of a MFE in reaction 48 has not been determined yet. (A MFE on sulfur-centered radical formation has been reported,[175,176] see section 5.)

No MFE (the experimental error was 2%, B = 1.25 T) has been found in the photodissociation of trichlorobromomethane in a benzene–toluene binary mixture.[177] The reaction probably proceeds via a singlet excited state.[177] Polydimethylsiloxanes have also been added to the reaction solution in order to increase its dynamic viscosity to $\eta \approx$ 100–200 cP. A RP containing

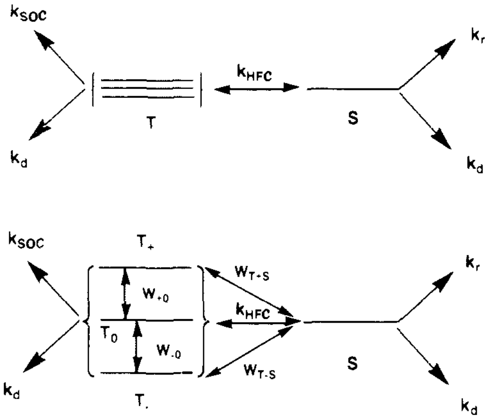
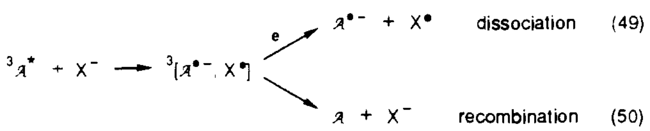


Figure 7. Schematic representation of interconnection between spin states of RP in a low ($B \approx 0$) (a) and in a strong ($B \gg A_{eff}$) (b) magnetic fields. All processes are considered as reactions of first order. k_r is the rate constant of formation of chemical product(s) (from refs 115, 146, 157, and 178).

a free radical heavy atom [$Br^•$,$^•CCl_3$] is formed in the reaction. The absence of MFE is related to a short electron spin relaxation time for $Br^•$, caused by the large SOC for this atom (cf. Table I).[13,177]

During the photolysis of dibenzyl ketone in SDS micelles a significant MFE on the formation of the cage product dibenzyl has been found, namely A = 68% (B = 14.5 T).[154] MFE's have also been found in the photolysis of *p*-fluoro and *p*-chlorodibenzyl ketone.[154] However, during the photolysis of *p*-bromodibenzyl ketone no MFE on the yield of a cage product has been found. In addition, the ^1H CIDNP generated by photolysis of the latter compound is also relatively weak compared to that found for dibenzyl ketone (see section 4.2).[154]

The photoreduction of dyes and certain other compounds in a triplet state ($^3\mathcal{A}^*$) by halides X^- (X^- = Cl^-, Br^-, I^-) results in the formation of triplet radical pairs $^3[\mathcal{A}^{•-},X^•]$, see eqs 42, 49 and 50. Experimentally



measured e values for these RP's are close to zero.[38,47] The reason for this is that strong SOC in the RP causes rapid T–S intersystem crossing, followed by a fast back-electron transfer in a cage.[38,47] These systems will be discussed in more detail in section 5 below.

MFE's on triplet RP's are often described within the framework of formal kinetics; in such a description all processes are considered first order as chemical reactions, see Figure 7.[5,113-115,145-147,157,178] In this procedure HFC-induced transitions have a rate constant $k_{HFC} = A_{eff}^{-1}$, where A_{eff} is the effective HFC constant of RP,[179] relaxation is characterized with $k_{rel} = T_1^{-1}$, etc. In a similar manner k_{SOC} has been introduced in refs 114, 145, and 178; k_{SOC} is the field- and nuclear-spin independent rate constant of T–S transition. Analysis of experimental A vs B dependencies enables one get more or less accurate estimation of k_{rel} and k_{SOC}.[114,145,157,178] This approach is evidently approximate and limited, but it conveys clearly the essence of events. For example, the $k_{rel}^{-1} = T_1$ values that are obtained are quite reasonable and are close to values obtained by ESR measurements.[113-115,157] The k_{SOC} values (k_{SOC} = 10^6–10^8 s^{-1}) obtained in such a way are larger for viscous liquids than for micelles,[114] cf. this section.

Triplet biradicals, where radical centers are interconnected with a methylene chain or by some other fragment, have relatively long lifetimes. Biradicals obtained by intramolecular photoreduction in a triplet state demonstrate significant MFE's.[180-185] The analysis of the effects as well as their field dependences enables one to conclude that the rate constant of biradical intersystem crossing is identified with a rate constant of biradical decay in the Earth's field which may be represented by a sum:[180]

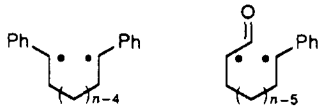
$$k_{obs} = k_{SOC} + k_{HFC} \qquad (51)$$

The observed rate constant k_{obs} depends on the flux density of the applied external magnetic field. For certain biradicals, the field dependence reaches a plateau for $B \gg A_{eff}$. The following holds true for k_{obs} for such high fields:

$$k_{obs} = k_{SOC} + {}^1/_3 k_{HFC} \qquad (52)$$

The use of these two equations enables one to estimate the relative contribution of field-independent SOC and field-dependent HFC to the decay of a biradical in any field.

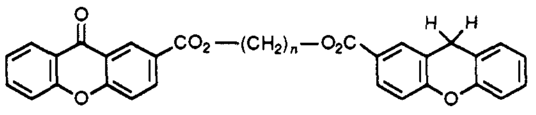
The comparison of data on dibenzyl and benzyl–acyl biradicals



where n = 6–15, shows that SOC plays a more significant role in benzyl–acyl biradicals, because density on an unpaired electron is high on acyl oxygen, and oxygen has a relatively large SOC constant ξ_A, see Table I.[53a,180,181] Therefore, the strong anisotropy of the g factor of the acyl radical also contributes to a large SOC effect.

The comparison of decay rates of 1,3-dibenzyl (n = 5), 1-benzyl-3-(*p*-chlorobenzyl), 1-benzyl-3-(*p*-bromobenzyl), and 1,3-bis(*p*-bromobenzyl) biradicals shows that the heavy atom (bromine) has a significant effect on the biradical decay; the relative decay rate constants for these biradicals vary as 1:1:3.3:4.8, respectively.[183]

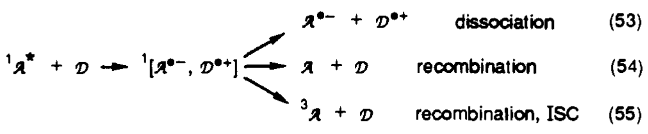
Much larger values of MFE's have been found in the study of intramolecular photooxidation/photoreduction of α-(9-oxoxanthen-2-yl)carbonyl]oxy]-ω-[(xanthen-2-ylcarbonyl)oxy]alkanes (XO-n-XH, n = 2–12).[185] Huge



XO-n-XH, n = 2–12

MFE's have been found, namely $k_{obs}(B = 0)/k_{obs}(B = 0.8\ T)$ = 15–19.[185] The reason for such a large effect for triplet biradicals lies in the absence of radical centers such as $-C^•{=}O$,[185] which are characterized by significant SOC and associated relaxation that tends to destroy the MFE,[7,184] see above.

A SOC effect has also been found for singlet ion-radical pairs (IRP's), which are formed during reductive quenching of photoexcited 9,10-dicyanoanthracene ($\mathcal{A}$) by donors ($\mathcal{D}$) aniline and *N*,*N*-dimethylaniline in acetonitrile.[186] The following reaction scheme represents the events:[186]



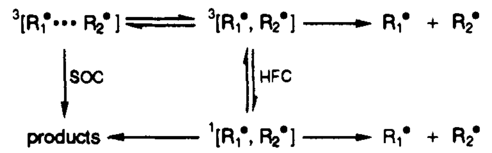
Parahalogenated (Cl, Br, I) donors have been used also. An increase of the Z value of the para substituent leads to an increase of the quantum yield of the triplet state (reaction 55).

It is worthwhile to mention in this section the MFE study in the dark oxidation reactions of 2,6-dialkylphenols into *p*-quinones and diphenoquinones catalyzed by Co(II) ($S = {}^3/_2; {}^1/_2$) and Mn(II) ($S = {}^5/_2$).[187-189] The singlet RP, which has a metal-centered radical is formed in a magnetosensitive step. The analysis of field dependences in the spirit of ref 180 (see above) enables one to estimate relative contributions of SOC and HFC to S–T evolution of the RP under investigation. The ratio varies over a wide range. For example, for the Co(II) ($S = {}^3/_2$) system, the SOC/HFC ratio is dependent on B and varies from 15/85 to 98/2.[187] Comparing these results with those for hydrocarbon biradicals,[180-183] one may claim that the MFE is quenched by heavy atoms Mn and Co. At the same time ISC of RP's containing metal-centered free radicals remains magnetosensitive.

This section closes with a summary of the data of the cage escape e and magnetic field effects A in the photogeneration of radicals via triplet states from precursors containing heavy atoms. The general observation, i.e., decrease of e_0 and decrease of A in the presence of a heavy atom, may be explained in the following way. In most cases SOC acts mainly in contact radical pairs (cf. section 2). Due to the fast SLR ($1/T_1 \gg |D_k|$), the triplet sublevels of the contact RP, or of a pertinent triplet intermediate (exciplex, biradical) rapidly interconvert. As a result, SOC induced T → S transitions lead to the decay of the triplet state as a whole (certainly, provided ($\sum_i k_{\mathrm{T}_i}S/3 > k_d$, where k_d is the dissociation constant). Consequently, the spin selectivity of a chemical reaction and thus MFE should be lost. Otherwise, under fulfillment of condition $1/T_1 \ll |D_k|$ one should expect the appearance of a MFE according to triplet mechanism, cf. section 3.2. A solvent viscosity increase leads to an increase in the lifetime of contact RPs (lowering k_d), and therefore, the probability of SOC-induced interconversion of triplet pairs into singlet pairs. As a result, the radical yield e_0 decreases in the Earth's field as the SOC increases in a system.

Analysis of the experimental data on *internal heavy atom effects* or SOC in (triplet) radical pairs can be rationalized by Scheme I or with a more refined Scheme II. Scheme II makes a distinction between contact and separated RP's,[113-115,157] cf. section 2.3. The contact RP may be considered as a complex or quasimolecule, similar to a biradical,[1] and the heavy atom effect is analogous to that found in the photochemistry of organic molecules.[7] So, it is believed that SOC-induced ISC leading to formation of "recombination" products takes place in contact RP's, see Scheme II. Quite similar considerations were applied in the description of the MFE in chemically-linked ion–radical pairs (IRP) formed by intramolecular electron transfer in a triplet state,[190] i.e., in a contact or "closed" triplet IRP SOC-induced direct electron transfer into the starting compound takes place, whereas in an "opened" IRP ISC according to HFC mechanism occurs.

Scheme II



The action of an external diamagnetic heavy atom may be related to modulation of the values and directions of the main axes of the **g** tensor of one of free radicals due to contacts with the heavy atom. The consequence of such contacts is the increase in the rate of paramagnetic relaxation in this radical, the loss of spin coherency in a system, and the decrease of the MFE, cf. section 4.1. At the same time, EHA can also stimulate the direct ISC in the contact RP's, biradicals, or exciplexes, and thus to decrease MFE. Diamagnetic EHA accelerates the T–S intersystem crossing in organic molecules.[7,21] One can expect that the same process is operative on the stage of transient intermediates (contact RP's, exciplexes, or biradicals).

4.4. Reactions of Radicals Containing Heavy Atoms in Random Pairs

The internal heavy atom effect can manifest itself also in reactions involving random pairs. Highly reactive particles with non-zero spins react in a liquid phase with the rate constant equal to the product of diffusion rate constant and spin-statistical factor σ:[191]

$$k = \sigma k_{\text{diff}} \tag{56}$$

In the case of reactivity anisotropy of reagent (reagents) the following more general formula holds true:

$$k = \sigma k_{\text{diff}} F \tag{57}$$

where $F < 1$ is the effective steric factor.[192]

Most organic radicals recombine (or disproportionate) as singlet pairs:

$${}^2\mathrm{R}^\cdot + {}^2\mathrm{R}^\cdot \xrightarrow{\sigma_1 k_{\text{diff}}} {}^1\mathrm{RR}\ [{}^1\mathrm{R}(-\mathrm{H}) + {}^1\mathrm{R}(+\mathrm{H})] \tag{58}$$

Provided that intersystem crossing of RP does not take place during the lifetime of the contact RP (the usual case for nonviscous media and absence of an internal heavy atoms, IHA), $\sigma = \sigma_1 = 1/4$. In the presence of significant SOC in one of the radicals caused by heavy atom and/or by peculiarities of its orbital structure, the spin prohibition in recombination can be partially or completely removed (${}^1/_4 < \sigma_1 \le 1$), and experimental values of $2k_{58}$ will be higher than ${}^1/_4 k_{\text{diff}}$. One possible reason for such an effect has been discussed above, i.e., mixing of states of different spin multiplicity in the contact RP or any intermediate–precursor of reaction products caused by SOC.

In a similar way, for a diffusion-controlled reaction between a free radical and molecular oxygen,leading to formation of peroxyl radical one has to expect $\sigma_2 = {}^1/_3$ provided interconversion between states of different multiplicity has no time to occur during the RP's

$$^2R^\bullet + {}^3O_2 \xrightarrow{\sigma_2 k_{diff}} {}^2RO_2^\bullet \tag{59}$$

lifetime. However, $^1/_3 < \sigma_2 < 1$ when effective SOC action operates.

In many cases the experimental values of σ for diffusion-controlled reactions 58 and 59 are equal within the accuracy of their determination to $^1/_4$ and $^1/_3$, respectively.[191-193] We shall consider below those few examples where σ exceeds the expected value ($^1/_4$ or $^1/_3$).

For recombination of pentacarbonylrhenium(0) in isooctane $2k_{60} = 5.4 \times 10^9$ M^{-1} s^{-1}.[194] This value exceeds

$$Re(CO)_5^\bullet + Re(CO)_5^\bullet \rightarrow Re_2(CO)_{10} \tag{60}$$

the corresponding value of $^1/_4 k_{diff} = 3.2 \times 10^9$ M^{-1} s^{-1}.[194] Following ref 195 one may state that, in recombination of metal(0) carbonyls, SOC reduces spin prohibition for recombination.

$2k_{58}$ values for organic radical recombination increase upon introduction of heavy atoms as substituents into their structure. Thus, in viscous solvents recombination constant $2k_{58}$ of ketyl free radicals of *p,p'*-dichlorobenzophenone; *p*-bromobenzophenone are 2–3 times higher than the rate constant of benzophenone ketyl radicals.[196]

Recombination of 1,3-dioxo-2-arylindan-2-yl free radicals and of a number of their derivatives is limited by diffusion.[197] The introduction of an iodine atom as a substituent into the structure of such a radical leads to a recombination rate increase of a factor of 1.5.[197] It is quite possible that such a variation in $2k_{58}$ is caused by a SOC increase in the system rather than by steric effects of the substituents.[196,197]

For the tri-*n*-butylstannyl free radical $(n\text{-}C_4H_9)_3Sn^\bullet$, k_{59} markedly exceeds $^1/_3 k_{diff}$; moreover, it is 3 times greater than k_{59} for a reaction of the radical of a similar structure centered on a lighter element, namely $(n\text{-}C_4H_9)_3Ge^\bullet$, cf. 7.5×10^9 and 2.5×10^9 M^{-1} s^{-1}, respectively (benzene, 300 K).[198]

The increase of σ in reactions of radicals with IHA's may be the result of SOC manifestation not only in contact RPs but, perhaps, appearing strange at first glance, in spatially-separated free radicals as well. Strictly speaking, the spin function for radicals characterized by significant SOC is not an eigenfunction of operators S_Z and S^2. As a result an α-spin state possesses an admixture of a β state. That is why in the very first moment of an encounter the random RP in the reaction 58 is neither pure triplet nor pure singlet. The statistical weight of a singlet state in a random RP increases and σ becomes more than $^1/_4$.[5,50] Besides that, the strong SOC-induced dynamic interconnection between α and β states determines the high rate of SLR in free radicals.[50,199] It has been mentioned already that a number of linear organic radicals such as $^\bullet$OH and $^\bullet N_3$ possess very large SOC, leading to their fast paramagnetic relaxation. It is not surprising that σ_1 = 1 for the reactions of OH$^\bullet$ + H$^\bullet$ and $^\bullet$OH + $^\bullet$OH[1] as well as for recombination of heavy iodine atoms.[192]

5. The Absence of a Strong Heavy Atom Effect

In section 3 we have discussed the existence of MFE's caused by SOC, and in section 4, the quenching of MFE's due to the same source. It is evident that there are situations when the presence of heavy atoms in a reactive compound does not manifest itself (as SOC) in experiments similar to those described above. In this section we shall describe and discuss such observations. Unfortunately, in a number of cases we are compelled to restrict ourselves to the observation of a specific and single magnetic field effect and are unable to compare its magnitude with any analogue without a heavy atom.

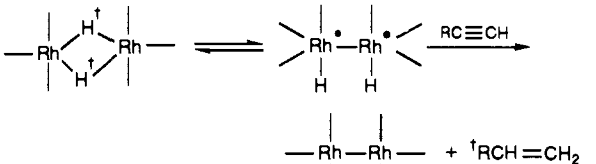
Both CIDNP and CIDEP phenomena in (photo)-chemical reactions are the result of the formation of radical pairs (or biradicals) a specific spin multiplicity, usually singlet or triplet, which is preserved for a certain time (typically 10^{-6}–10^{-9} s).[66] The existence of CIDNP and CIDEP in (photo)reactions of organoelemental compounds[200] indicates that RP's of a certain multiplicity $[R^\bullet, {}^\bullet ER_n]$ are formed. Special attention should be paid to the polarized radicals (CIDEP) or polarized reaction products (CIDNP) which are formed with participation of such pairs $[R^\bullet, {}^\bullet ER_n]$, and not in other radical pairs. Observation of the MFE and, moreover, a MIE are the conclusive indications of magnetosensitivity of a free radical reaction under investigation.

Table V presents references to publications dealing with magnetic and spin effects in reactions of element-[200] or metal-centered free radicals. We shall consider below some of these experimental observations in more detail.

5.1. CIDNP in Free-Radical Reactions of Compounds with Heavy Atoms

^{15}N, ^{19}F, and ^{31}P CIDNP are routinely measurable in research in modern physical organic chemistry, and it is known that there is no reason to pay special attention to the role of SOC in RP with radicals containing N, F, or P atoms.[201,202]

It was mentioned in section 4.2 that weak ^{1}H CIDNP has been observed in photochemical reactions proceeding with the formation of metal-centered radicals, in particular UO_2^+.[155,203] Further, ^{1}H CIDNP which is created in the conjugated metal-centered biradical of such a heavy metal as rhodium (Z = 45) has been found:[204]



(61)

A biradical reacts in a triplet state with the formation of vinyl products. Both hydrogen atoms of the starting compound as well as of vinyl products show CIDNP.[204]

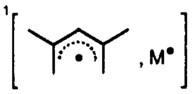
^{1}H CIDNP was observed in chemical reactions of $HMn(CO)_5$ and $HCo(CO)_5$ (both denoted as HM) in

Table IV. Inorganic Ions, Corresponding Free Radicals, Their Electronic Terms, and Cage-Escape Estimates of the Radicals from Triplet Radical Pairs[a]

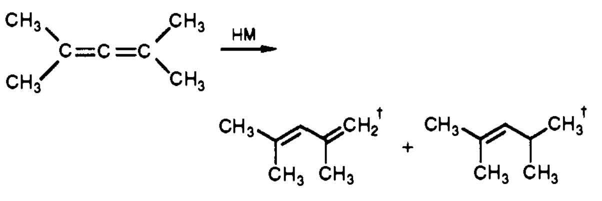
anion	radical	term	e_0
NO_2^-	$NO_2^•$	$^2A_1$	>0
N_3^-	$N_3^•$	$^2\Pi_g$	≤0.1
CO_3^{2-}	$CO_3^{•-}$	$^2A_1'$	>0
^-OH	$^•OH$	$^2\Pi$	≈0
NCS^-	$^•NCS$	$^2\Pi$	≈0
$2NCS^-$	$(NCS)_2^{•-}$		>0
SO_3^{2-}	$SO_3^{•-}$	$^2A_1$	>0

[a] Data of refs 38, 47, and 48.

reactions with conjugated hydrocarbons, which produce the RP



where M$^•$ is the metal-centered radical.[205] The reaction with tetramethylallene leads to the formation of two compounds which exhibit ^{1}H CIDNP signals.[205]



(62)

Both ^{1}H CIDNP and MFE were observed in reactions proceeding via the formation of a singlet RP containing the triethylgermyl radical;[206] ^{1}H CIDNP was found in reactions of benzoyltriethylsilanes.[206b] Analysis of ^{1}H CIDNP data in these reactions of Ge- and Si-centered radicals shows that the influence of SOC is insignificant.[206b]

^{1}H CIDNP signals were observed in the photoreaction of *p*-chlorobenzophenonemercury in acetone-d_6 in the presence of 2-propanol.[207] ^{1}H CIDNP under photolysis of diphenylmercury has been observed[208]

The data on ^{1}H CIDNP in the reactions of trimethyltin hydride, where both magnetic ^{117}Sn and nonmagnetic ^{118}Sn isotopes have been used, are of particular interest.[209] The ^{1}H CIDNP created in RP of [$\equiv$^{117}Sn$^•$, R$^•$], where HFC is large, and in RP of [$\equiv$ ^{118}Sn$^•$, R$^•$], where HFC is small, was observed.[209] One may expect the quenching action of SOC, but it does not occur. This result convincingly shows the negligible role of SOC in S–T interconversion of the RP under consideration.[209]

Table V. Experimental Observation of Magnetic and Spin Effects in Reactions of Element- and Metal-Centered Free Radicals[a]

element	*Z*	^{1}H CIDNP[b]	CIDEP	MFE[c]	MIE
O	8	210	211	157, 171, 212	214a
Mg	12	215, 228, 229, 231			
Si	14	206b, 216	217		214b
P	15	201[d]	57, 218	111	
S	16	176	176	175, 176	176, 219
Mn	25	205, 220, 221, 224b		187, 188	
Fe	26	215, 220, 229, 231, 254a			
Co	27	205, 222–224a	225	101,[e] 102,[f] 187, 189, 254b[g]	
Cu	29	228		95	
Zn	30	206b, 216			
Ge	32	232	240	169, 170, 206	
Zr	40				
Ru	44			49,[h] 51,[h] 102,[f] 103,[h] 233	
Rh	45	204		100[e]	
Pd	46	234			
Sn	50	206b, 209, 235			
Pt	78	234, 235			
Au	79	235			
Hg	80	207, 208, 228			
Pb	82	235			
U	92	155, 156, 203	236[i]	92,[h] 156	156, 203b, 237

[a] We do not consider magnetic and spin effects in C-centered and other radicals centered on elements lighter than O. [b] ^{1}H CIDNP signals were observed in (photo)reactions of organoelemental compounds. There is no comprehensive evidence for creation of polarization in pairs [R$_1^•$,$^•$*E*R] in most cases; cf. original publications. [c] Mainly positive MFE due to the dominant action of a HFC mechanism in triplet RP's was observed. [d] ^{31}P CIDNP was observed. [e] Strong positive MFE (A ≈ 100%, *B* = 2.4 T). [f] Complex nonmonotonic field dependence of outer-sphere electron-transfer reactions between coordination complexes. [g] Negative MFE was observed in photogenerated singlet RP's. [h] Negative MFE due to the dominant action of TM, Δg or a "hybrid" mechanisms was observed. [i] CIDEP of stable nitroxyl radical interacting with photoexcited uranyl salt was observed.

Table VI. Possible Interactions that Can Trigger ISC and IC in Radical Pairs and Biradicals

symbol	interaction	comments
ξ_h	spin–orbit coupling	$\{T_i \leftrightarrow T_j\}$, $T_i \leftrightarrow S$
Δg	$\omega_0 \Delta g$, Zeeman	$S \leftrightarrow T_0$ only
A_{eff}	hyperfine coupling	$T_i \leftrightarrow S$
$T_{1,2}$	paramagnetic relaxation induced by (1) **g** anisotropy, (2) **A** anisotropy, (3) spin–rotational interaction, (4) Coulomb field of nearest neighbors	$\{T_i \leftrightarrow T_j\}$, $T_i \leftrightarrow S$

The data on ^{1}H CIDNP in reactions of heavy metal-centered free radicals such as radicals of sodium (*Z* = 11), magnesium (*Z* = 12), manganese (*Z* = 25), zinc (*Z* = 30), zirconium (*Z* = 40), molybdenum (*Z* = 42), palladium (*Z* = 46) in (*Z* = 50), platinum (*Z* = 78), gold (*Z* = 79), mercury (*Z* = 80), lead (*Z* = 82) has been reviewed.[149] Despite a number of complications in the interpretation of the data it seems possible that in certain cases polarization is formed in the RP's, in which one of constituents is a metal-centered free radical.[149] However, the main problem in such experiments is to prove that the CIDNP is actually created in those RP's containing metal-centered free radicals. Table V summarizes observed of ^{1}H CIDNP in reactions of organoelemental compounds.

5.2. CIDEP in Photoinduced Reactions of Compounds with Heavy Atoms

There are a limited number of publications on CIDEP in photochemical reactions proceeding with the formation of heavy element- or metal-centered free radicals (cf. Table V); most of them will be considered below. For example, strong CIDEP signals of ^{31}P-centered free radicals have been observed, see Figure 8. (The symbol "#" is used in Figure 8 and in the text below for designation of electron polarization.)

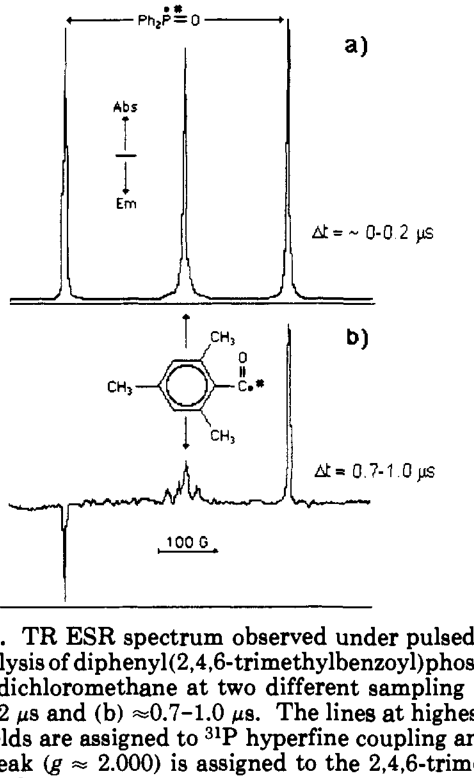
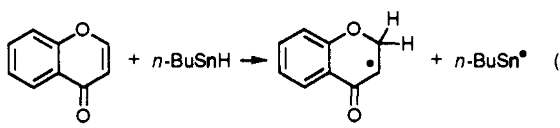


Figure 8. TR ESR spectrum observed under pulsed ($\approx$20 ns) photolysis of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide in dichloromethane at two different sampling gates: (a) $\approx$0–0.2 μs and (b) $\approx$0.7–1.0 μs. The lines at highest and lowest fields are assigned to ^{31}P hyperfine coupling and the central peak ($g \approx 2.000$) is assigned to the 2,4,6-trimethylbenzoyl radical (from ref 57).

Hayashi, Sakaguchi, et al.[3a,230,238-240] studied CIDEP generated in the photoreduction of aromatic carbonyl compounds in the π,π^*-triplet state by silicon ($Z = 14$), germanium ($Z = 32$), and tin ($Z = 50$) compounds. The following donors were used: Ph_3SiH, Ph_3GeH, Me_3SnH, *n*-Bu_3SnH, Ph_3SnH, general formula R_3EH. The



(63)

photoreduction reaction leads to formation of a primary pair $[R_1^\bullet, ^\bullet ER_3]$, where $R_1^\bullet$ happens to be cyclohexadienyl and not ketyl radical. The hydride-type donors, where hydrogen atom has negative charge avoids reaction with negatively charged carbonyl oxygen.[230] In the case of silicon containing compounds the hydrogen abstraction from the hydrocarbon substituent with formation of a C-centered free radical took place.[241] Polarized cyclohexadienyl radicals were observed in all cases.[3a,230,238-240]

Weak polarization of $Ph_3Ge^\bullet$ was observed.[3a,240] No CIDEP was observed in the case of tin-centered free radicals.[230,239,241] The reason for the absence of CIDEP signals in the $R_3Sn^\bullet$ radical can be related to the fast paramagnetic relaxation induced by SOC within the radical.[239] Another possible mode of relaxation is the very fast degenerate hydrogen atom exchange with a rate competitive with SLR:[239,242]

$$R_3Sn^\bullet + R_3SnH \rightarrow R_3SnH + R_3Sn^\bullet \quad (64)$$

The photolysis of methylaquacobalto–oxime $CH_3Co(CH_3)(NOH)C(NO)(CH_3)_2(H_2O)$ in water and 2-propanol results in the observation of strongly polarized methyl radicals.[225] The polarization is produced mainly by a triplet mechanism (TM) (99%) with a small contribution of a radical-pair mechanism (1%).[225] The counter radical of the methyl radical is diaquocobalto–oxime, a Co-centered ($I = {}^7/_2$, $Z = 27$) free radical.[225]

Photoinduced electron transfer between photoexcited zinc tetraphenylporphyrin (ZnTPP, $Z = 30$) in a triplet state and benzoquinone-1,4 (BQ) or duroquinone (DQ) was studied by time-resolved (TR) ESR and Fourier transform (FT) ESR.[226,227,243-246] CIDEP signals of both

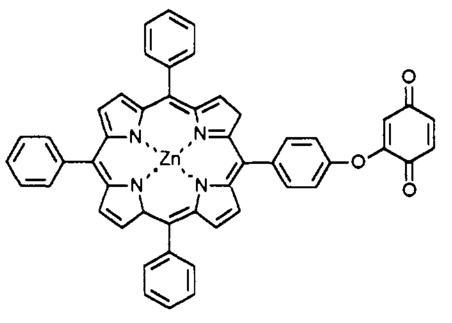
$$^3ZnTPP + BQ \rightarrow ZnTPP^{\bullet+} + BQ^{\bullet-} \quad (65)$$

radical–cation and radical–anion were observed.[243,246] Deuterium labeling of porphyrine (ZnTPP-d_{20}) leads to the enhancement of the spectral resolution of the spectrum of the porphyrine radical–cation by reducing the broadening caused by unresolved proton HFC's.[243,246] The CIDEP is explained as the simultaneous action of TM and the radical pair mechanism (RPM).[227,243,246] A CIDEP was also observed when MgTPP ($Z = 12$) or MgTPP-d_{20} was used instead of ZnTPP.[246] The role of a heavy atom Zn here seems to be negligible because the radical–cation of $ZnTPP^{\bullet+}$ shows very small HFC on $_{30}Zn^{67}$ (ca. 0.1 mT[37]), i.e., this is basically not a zinc, but a nitrogen-centered free radical. This is an instructive case of the "remote heavy atom" effect. A very similar case was considered in section 3.1 for the $Ru(dce)_3^+$ radical.

At the same time the heavy atom has a striking effect on the sign of CIDEP according to TM in reactions with Mg TPP and ZnTPP.[244,245] The TM gives enhanced absorption for ZnTPP/DQ and emission for MgTPP/DQ reflecting changes in relative rates of triplet sublevel populations.[244,245]

In a few cases the FT technique has been employed to investigate CIDEP[226,227,244,245] in photoreacitons of porphyrins with quinones described above. Only the free-induction decay signals of quinone radical–anions were observed in these FT ESR experiments because $ZnTPP^{\bullet+}$ has a short T_2.[226,227] There are no reasons to ascribe this short T_2 to the presence of a heavy Zn atom.

Photoinduced electron transfer in the covalently linked zinc tetraphenylporphyrin quinone diad (ZnTPQ) in ethanol at low temperatures (130–160 K) leads to the formation of an ion-radical pair (IRP).[247] These IRP's show CIDEP due to the TM and by spin-correlated radical pair mechanism.[152,247]



ZnTPQ

Polarized ESR signals of silicon-centered free radicals (^{29}Si) were observed in reactions of alkylsilanes with *tert*-butoxyl free radicals.[217]

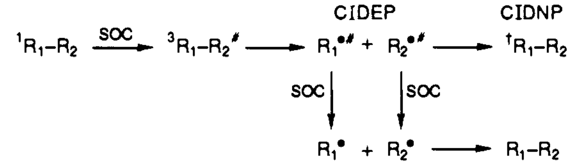
Attempts to observe CIDEP of organic free radicals produced in the photoreduction of photoexcited uranyl were unsuccessful.[236] CIDEP signals of a stable free radical 4-(trimethylammonio)-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO$^+$) nitrate were observed upon quenching of photoexcited uranyl salts in solutions of polyelectrolite, i.e., sodium poly(styrenesulfonate).[236]

$$\mathrm{UO_2}^{2+*} + \mathrm{TEMPO}^+ \xrightarrow{\mathrm{NaPSS}} \mathrm{UO_2}^{2+} + \mathrm{TEMPO}^{+\#} \qquad (66)$$

The results were in agreement with the nominal triplet multiplicity of the photoexcited uranyl ion.

Scheme III summarizes the two-way action of SOC in the generation and quenching of CIDEP and CIDNP (sections 5.1 and 5.2) according to the triplet mechanism (TM). The SOC-induced S–T interconversion leads to a selective population of triplet sublevels in the reactive molecule. The photodissociation of this molecule leads to CIDEP signals according to TM of the radicals formed, as well as CIDNP signals of recombination products generated by the usual nuclear polarization mechanisms. At the same time the strong SOC in free radicals leads to enhanced paramagnetic relaxation (section 4.1) and can wash out both electron polarization on the radical stage of reaction and the creation of the nuclear polarization in reaction products. The experimentally observed polarizations are the result of competition between these two SOC-induced processes.

Scheme III

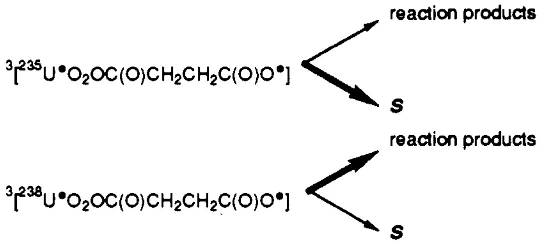


5.3. Magnetic Isotope Effects

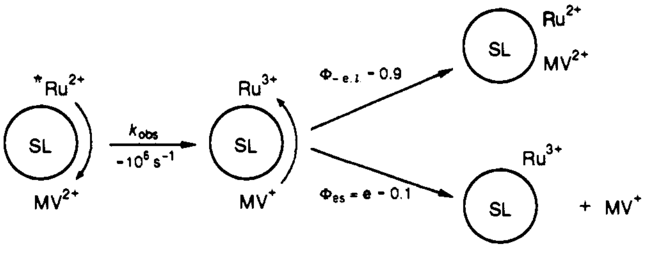
The magnetic isotope effect (MIE) is one of the most interesting magnetic and spin effects and demonstrates that different rates of elementary reactions of radical pairs containing different magnetic isotopomers can occur. This effect comes from the difference in nuclear spin but not in nuclear charge or mass.[1,3,156,213] MIE was observed for four elements heavier than carbon, namely, oxygen, silicon, sulfur, and uranium, cf. Table V. The search for MIE in tin[242,248] appears not to have been successful. Detailed discussions of the MIE can be found in recent publications.[3,156,213]

Uranium is the heaviest element in which the MIE was documented.[156,203b,237] In order to obtain favorable conditions for MIE action, the photolysis of uranyl succinate (*S*) was studied.[203b] The reaction is supposed to involve triplet biradical formation; see Scheme IV. The T–S-intersystem crossing in a biradical should be faster in the presence of the magnetic isotope ^{235}U than in the presence of the nonmagnetic ^{238}U. For this reason the enrichment with ^{235}U isotope of *S* during photolysis can be expected. In fact, analysis showed that *S* which contained 30% of ^{235}U became enriched in ^{235}U isotope up to 6 ± 1% at 85–90% conversion. MIE is the most probable reason for the enrichment.[203b]

Scheme IV



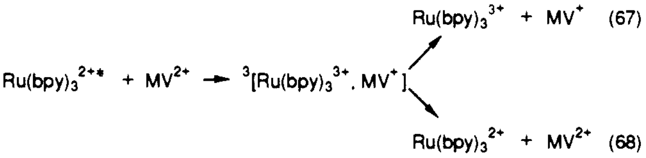
Scheme V



The SOC constant of an atom for which MIE was found varies from ξ_A = 151 (oxygen) to ξ_A = 2000 cm^{-1} (uranium, Table I). However, the efficiency of the MIE does not change much in this series. That means that the ξ_A constant of an atom does not adequately represent the ability of SOC in a system to quench spin and magnetic effects (see also section 5.4 below). In relation to this, the knowledge of the energy of interaction of an unpaired electron with a magnetic nucleus of element (HFC constant) and principal values of **g** tensor of element-centered free radicals is highly desirable for better understanding of MIE.

5.4. Miscellaneous

The study of the MFE's in reactions involving RP's, where one of the radicals is produced from a transition metal complex of high symmetry is of obvious interest. In such a system SOC is often very effective due to the high nuclear charge and the partially unquenched orbital angular momentum of the d-shell electrons. The kinetics of electron transfer between photoexcited Ru(bpy)$_3^{2+}$ and *N,N'*-dimethyl viologen (MV^{2+}) has been studied by means of laser flash photolysis in SDS and sodium laurate (SL) micelles.[233] Analysis of the data showed that the quenching is mainly intramicellar. Although SDS solutions show no escape of radicals MV$^+$ and Ru(bpy)$_3^{3+}$ from the micelles, for solutions of SL micelles an escape value e$_0$ ≈ 0.1 was observed; see the Scheme V. The dependence of e$_0$ on the concentration of SL and SDS shows a drop in the vicinity of the c.m.c. The product radical MV$^+$ is not incorporated into the SL micells. An increase of e in the SL micelles up to A = 20–25% was observed with the application of an external magnetic field (0.2–0.47 T) in steady-state irradiation and laser flash photolysis studies. The magnetic field effect is consistent with a dominant



$$\mathrm{Ru(bpy)_3}^{2+*} + \mathrm{MV}^{2+} \rightarrow {}^3[\mathrm{Ru(bpy)_3}^{3+}, \mathrm{MV}^+] \rightarrow \mathrm{Ru(bpy)_3}^{3+} + \mathrm{MV}^+ \qquad (67)$$

$$\phantom{\mathrm{Ru(bpy)_3}^{2+*} + \mathrm{MV}^{2+} \rightarrow {}^3[\mathrm{Ru(bpy)_3}^{3+}, \mathrm{MV}^+]} \rightarrow \mathrm{Ru(bpy)_3}^{2+} + \mathrm{MV}^{2+} \qquad (68)$$

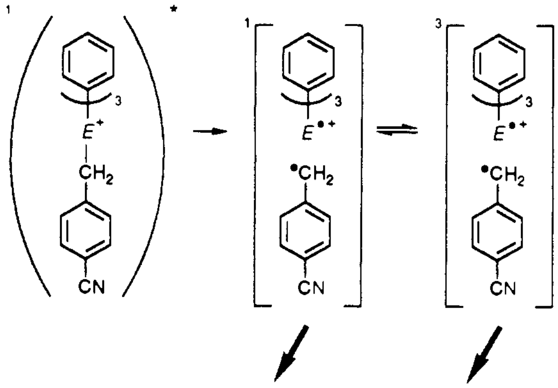
hyperfine coupling (HFC) mechanism. Geminate recombination kinetics of the pair $^3[MV^+,Ru(bpy)_3^{3+}]$ were investigated in SDS and SL micelles.[233]

A serious objection to the assignment of the HFC to explain the MFE in this system is the strong anisotropy of the g factor of $Ru(bpy)_3^{3+}$ (cf. section 2.3), which should result in fast paramagnetic relaxation of RP's and which can diminish or completely destroy any MFE. However, in a crystalline form or in a microenvironment (such as a zeolite), which can lower the crystal field symmetry of a complex, Ru^{3+} complexes demonstrate ESR signals even at room temperature.[249] The lowering of crystal field symmetry leads to an increase of d-orbital splitting and thus to the hindering of the SLR process (see section 4.1). Thus, conditions can be found such that paramagnetic Ru complexes do not experience extremely fast paramagnetic relaxation. It is quite possible that $Ru(bpy)_3^{3+}$ localized on a surface of a micelle also possesses a relatively long spin relaxation ($T_1 \geq 10^{-7}$ s), which would explain the ability of HFC to induce the observed MFE. A possible alternative explanation is that the observed MFE is the result of some unknown secondary RP which does not involve $Ru(bpy)_3^{3+}$, but which consists of MV^+ and an unidentified organic radical.[250,251]

Although the reaction (eqs 67 and 68) between $Ru(bpy)_3^{3+}$ and MV^+ displays a *positive* MFE (resulting from a HFC mechanism) when the reaction is conducted in micellar systems, the same reaction displays a *negative* MFE (resulting from TM, Δg mechanism or a "hybrid" mechanism) in homogeneous liquids or low or moderate viscosity (see section 3.3). Similar behavior for triplet RP's has also been found for reactions which show pronounced negative MFE in homogeneous solutions due to a triplet mechanism, but when run in micelles, show a very weak negative MFE or a positive MFE due to favorable conditions for the occurrence of a HFC mechanism due to the enhanced lifetime and repeated reencounters of the RP.[112] Thus, the HFC mechanism in micellar solutions generally dominates the triplet mechanism.[233]

A MFE on the yield of products of reaction 67 in aqueous solutions in a rather strong field, B = 2–4 T, was first been reported by Ferraudi and Argüello.[103] They attributed the observed MFE to a field-induced reduction of the *forward* electron-transfer process.[103] However, this interpretation is at variance with a more detailed kinetic analysis based on the results of nanosecond time-resolved laser flash spectroscopy.[49,51,233] It has been shown, that in this reaction the MFE on the yield of free radicals is due to the influence of the external magnetic field on the fast *back*-electron transfer in the primary pair of redox products.[49,51,233]

The competition of certain reactions of the same RP's, consisting of radicals centered on elements (E) of the V-th group (N, P, As) as well as on the elements on the VI-th group, e.g., S, has been investigated.[252] Photolysis of salts of aryl ammonium, aryl phosphonium and aryl arsonium in acetonitrile led to the formation of a singlet RP, which may give cage products or undergo interconversion into triplet state and yield out-of-cage products. In the case of E = P and As the reaction proceeds the following way:



(69)

It was found that the higher the HFC constant on the heteroatom E in the element-centered radical formed, the larger the rate of interconversion into triplet RP and the smaller the fraction of cage products.[252] The variations in the product yields are not related to the atomic number Z of the heavy element. These facts enabled the authors of ref 252 to conclude that SOC makes an insignificant contribution, since it would grow strongly in the order of N, P, S, and As. This observation is in accordance with the weak dependence of the MIE value on atomic number, see section 5.3.

MFE's were observed for phosphorus- and sulfur-centered radicals,[111,175,176] see Table V. Namely, photolysis of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide as well as phenacyl phenyl sulfone in SDS micelles led to triplet radical pairs, consisting of a benzoyl radical together with either a diphenylphosphonyl $Ph_2P^{\bullet}{=}O$[111] or benzenesulfonyl $PhS^{\bullet}O_2$[175] radical. The application of a strong magnetif field (B = 1.2 T in both cases) led to an increase of the RP's lifetime. It was found for the RP with S-centered radical $A = 53 \pm 5\%$.[175]

From the above example and from data of Table V, it is clear that the simple occurrence of a heavy atom possessing a large value of ξ_A in a radical pair by no means guarantees that SOC will operate in an effective manner to influence the spin dynamics of the system containing the atom. The *first* requirement for the efficient operation of SOC is a high spin density on the heavy atom (see above). Support for this requirement can be found in ref 49, see section 3.2. It has been already mentioned that in the course of photoreduction of $Ru(dce)_3^{2+}$ by substituted anilines a RP containing $Ru(dce)_3^{+}$ is formed. Despite the presence of the heavy atom Ru, the triplet mechanism in the (exciplex) RP only operates when a heavy atom (iodine) is introduced into the structure of the reacting partner, namely when the reducing agent is p-iodoaniline.[49] The reason for the inactivity of heavy atom Ru in introducing SOC can be understood as follows. In the photoreduction of $[Ru(II)(dce)_3]^{2+}$ an electron, roughly speaking, is transferred to the ligand, and the reduced complex has the structure $[Ru(II)(dce)_2(dce)^{-}]^{2+}$. Such a representation leads to the expectation that the g factor for the excited complex should possess a value close to the g factors for organic free radicals, whereas the g factor of another Ru radical, $Ru(bpy)_3^{3+}$, for which the odd electron is associated strongly with the metal center, has components of **g** tensor which differ up to ~0.6 from g_e.[39,49] Thus, strong SOC in a heavy atom, as reflected by the magnitude of the ξ_A constant (see Table I and section 2), does not necessarily mean significant SOC in a radical or in an excited intermediate complex containing this astom, when the spin density on the atom is low.

In addition to the requirement of a significant spin density on a heavy atom possessing a large value of ξ_A, the *second* requirement for the manifestation of a strong contribution of SOC is that the energy Δ in the compound containing the heavy atom must be low ($\Delta \approx \xi$), otherwise small and ineffective SOC will result. As an example illustrating the last statement, one can consider the complex of potassium diplatinate $K_4[Pt_2H_8P_8O_{20}]\cdot 2H_2O$ ($[Pt_2(pop)_4]^{4-}$),[17] which possesses a very large value of ξ_A constant for Pt ($\xi_A = 4000$ cm^{-1}, Table I). However, from the luminescence measurements of this complex at $T < 9$ K, the energy of SOC in this system was estimated as only 40–50 cm^{-1}, due to the strong suppression or orbital momentum by the electric field of the ligands attached to Pt.[17] Moreover, Coulomb interaction of any pair of atoms, which leads to the formation of a diatomic molecule (or "diatomic like" pairing between heavy atoms within polyatomic system) with $\mathbf{L}_Z = 0$ will result in the strong diminution of the SOC energy in the system relative to that present in the pair of spatially well-separated atoms, irrespective of the magnitude of ξ_A (or the atomic number Z) in the individual atom (see section 2.2.1). If similar conditions occur for exciplexes and contact RP's, the action of SOC will be insignificant despite the presence of heavy atom(s) possessing large values of ξ_A and high spin densities on the heavy atom.

Some convincing examples, which corroborate these considerations, are photoreduction reactions of triplet carbonyl compounds and dyes by simple inorganic ions including halides,[38,47,48] eqs 42 and 49 (see section 4.3). It is supposed that the cage recombination efficiency (competition between reactions 49 and 50) is determined mainly by SOC. In systems where halogen atoms (atomic radicals) are generated (the ground state of a halogen atom is $^2P_{3/2}$, orbital momentum $L = 1$), SOC is large and therefore $e \approx 0$. However, with an increase of alkali halide concentration reaction 70 can occur

$$X^\bullet + X^- \rightarrow X_2^{\bullet -} \qquad (70)$$

during the pair's lifetime. The diatomic radicals produced in reaction 70 have quite a different orbital configuration than the halogen atomic radicals $X^\bullet$ (cf. Table II), namely the ground state of X_2^- is $^2\Sigma_u^+$ and average orbital momentum is zero ($\Lambda = 0$). Thus, analogous to the case of $[Pt_2(pop)_4]^{4-}$, despite an increase in the number of heavy atoms in a species, the effective SOC energy in the united system is small, and the SOC-induced spin relaxation is decreased relative to the atom. Hence radicals may avoid recombination and exit from the cage ($e > 0$).[253]

So, it should be expected that, in cases where linear radicals with $\Lambda = 0$ and $\xi/\Delta \ll 1$ are formed, $e > 0$.

The same considerations hold true for a number of simple polyatomic anions, which quench the triplet states with the formation of exciplexes or RP's.[38,47,48] The strong dependence of an estimated magnitude of e upon the angular momentum, reflected by the radical ground electronic term, can be seen from Table IV.

Organic radicals do not exit from the cage ($e \approx 0$) during the reductive quenching of triplets by ferrocyanide.[38] It has been proposed that the reason for the

$$^3\mathcal{A}^* + Fe(CN)_6^{4-} \rightarrow {}^3[A^{\bullet -}, Fe(CN)_6^{3-}] \rightarrow \mathcal{A} + Fe(CN)_6^{4-} \qquad (71)$$

high cage effect (no radical escape) is that ferricyanide $Fe(CN)_6^{3-}$ is formed in the configuration $^2T_{2g}$ ($L \neq 0$), which is characterized by a strong effective SOC.[38] This is the origin of the efficient recombination in the pair.

All of the examples presented above demonstrate the important role of SOC *in a radical pair* and are a demonstration of a concept of IRSOC proposed in ref 38, cf. section 2.3.

The external heavy atom (EHA) effect or external spin–orbit effects also do not always manifest themselves in magnetic and spin effects; they may be camouflaged by more significant "chemical" or "physical" effects related to the introduction of compounds with heavy atoms. For example, the replacement of hydrocarbon, alcohol, or any other solvent not containing heavy atoms by a solvent consisting of halogen-substituted molecules, results in a variation of parameters of the ESR spectrum of the stable radical due to a normal solvent effect (solvation ability, polarity, etc.).[135]

It was already mentioned in section 4.1.3 that salts of lanthanides (Z = 58–71, 4f elements) and of 3d elements in micellar and homogeneous solutions may quench MFE's.[136–138,144,254] However, the efficiency of this quenching does not correlate with Z, but with the value of the total angular momentum of the electron of the lanthanide ion[136–138,254] (see section 4.1.3). Furthermore, it was shown that salts did not influence the rate of exit of radicals from the micellar cage in the absence of a field.[136–139] The reason for the MFE quenching seems to lie in the effective spin exchange between the metal ion and a radical of the geminate RP; this exchange leads to rapid relaxation in the triplet manifold and to the loss of spin coherence in the RP, and counteracts the influence of an external field on splitting the three triplet sublevels.[136–139,144] The same phenomenon, i.e., spin exchange, is probably the reason for the great decrease of the triplet biradical lifetime in the presence of lanthanide ions.[140]

Spin relaxation induced by exchange interaction, is usually accompanied by relaxation process induced by magnetic dipole interaction (e.g. between a paramagnetic complex and a radical). Dipole–dipole interaction gradually decreases with distance R (as R^{-3}) between magnetic dipoles (i.e., between radical and paramagnetic complex in our case), whereas exchange interaction exponentially decreases with distance. Thus SLR induced by dipole–dipole interaction in spatially well-separated RP's obviously dominates the contribution of the exchange mechanism. The importance of the magnetic dipole interaction in the quenching of MFE's by lanthanide ions has been demonstrated in ref 140 for biradicals and in ref 143 for chemically linked RP. The presence of a permanent magnetic dipole of metal ions masked the possible role of SOC enhancement in the system in the process of MFE's quenching by EHA. The introduction of diamagnetic salts of heavy elements (La^{3+} and Lu^{3+}) to micellar systems does not result in effects exhibited by lanthanide ions possessing net spin, except for the trivial effect of the variation of the micelle's structure resulting from the presence of salts in relatively high concentrations,[148,255] see also section 4.1.3.

The role of SOC in stimulated nuclear polarization (SNP) in relative biradicals was studied in ref 256. SNP is a modern technique based on the effect of a resonance microwave field on the singlet–triplet evolution of RP's or biradicals.[257] The simulation of SNP spectra of biradicals demonstrates that the intensity of the spectrum is not affected by spin–orbit interaction for systems characterized by the rate constants approaching $k_{SOC} \approx 10^7$ s^{-1} (cf. section 4.3), whereas further increase in the value of k_{SOC} leads to a decrease of the spectrum intensity.[256]

New MFE has been observed recently on reactivity of RP of two atoms [Cl$^•$, Cl$^•$] in solid phase at 77 K.[258] There are no definite spin states of such RP due to unquenched orbital momentum of the Cl atom and its large effective SOC constant ξ_A (Table I); only Ω is a good quantum number. The transitions between repulsive and attractive terms of Cl···Cl induced by HFC of chlorine atom were suggested to be the origin of observed MFE.[258] Such a mechanism is analogous in a sense to S–T$_-$ mechanism of ISC in RP's with definite spin states.[1,151,258] Further evidence for such a promising mechanism of MFE's in systems with strong SOC would be welcome.

6. Spin–Orbit Coupling and Classification of Magnetic Field Effects

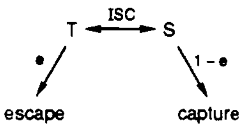
We have tried to demonstrate in this review that SOC has diverse manifestations in magnetic and spin effects in reactions involving radicals. We briefly summarize these manifestaions below and present *experimental criteria* for discovery of the operation of SOC in chemical phenomena.

For an individual free radical with near-degenerate orbitals ($\Delta \le \xi$) the SOC most obviously manifests itself in the marked deviation of components in their **g** tensor from the value for a free electron g_e. Such radicals often possess an intrinsic anisotropy of **g** tensor and are characterized by a fast paramagnetic relaxation (short $T_{1,2}$). Short $T_{1,2}$ times tend to rapidly equilibrate electronic spin systems and lead to a decrease of MFE's involving geminate radicals pairs. At the same time, a difference between g factors of free radicals provided another origin of MFE, namely MFE according to the Δg mechanism.

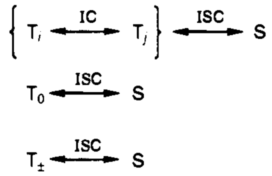
The triplet mechanism of MFEs may also be considered as a result of anisotropy of SOC. Anisotropic SOC leads to predominant population ($S_1 \rightarrow T_i$) and deactivation ($T_i \rightarrow S_0$) of certain zero-field sublevels of a reactive triplet molecule (or exciplex). The Δg, "triplet" and "hybrid" mechanisms of MFE all lead to *negative* MFE values ($A < 0$), cf. section 3.

The action of SOC in triplet RP's (IRP's, biradicals), demonstrating positive MFE $A \ge 0$, has been widely discussed in the current literature, cf. section 4. A statement on the significant operation of SOC in such systems is usually made in a deductive manner, i.e., conclusions are based not on direct experimental measurements of this interaction, but rather on consideration of its manifestation in other measurable parameters and their comparison with similar molecular systems, where no action of SOC is believed to operate. The arguments for action of SOC that can be found in publications vary widely in their ability to be convincing.

Scheme VI



Scheme VII



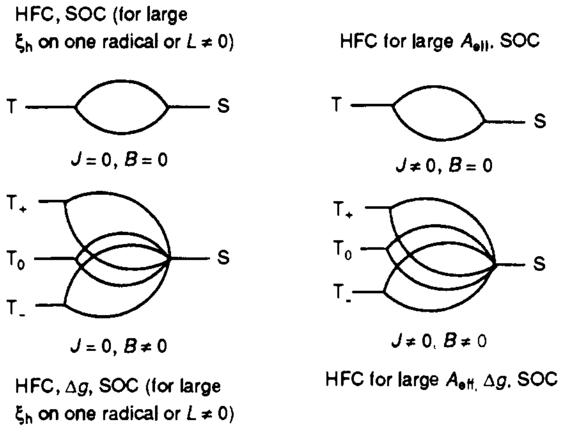
In the case of positive MFE's in triplet RP (or IRP's or biradicals), the following experimental criteria can be used in order to claim the occurrence of SOC-induced S–T interconversion of RP: (a) a smaller magnitude of MFE's values in comparison with a system of similar chemical structure but "without strong SOC action" (similar A_{eff}, similar solvent viscosity or the same micelles, the same magnetic flux density of external field, etc.); (b) evidence of an appreciable spin density on the heavy atom in a partner(s) in RP and/or structural peculiarities leading to non-zero orbital momentum of either partner of RP; (c) the increase of e value to less than 66% ($^2/_3$) under the application of a high MF. (Provided the field dependence of MFE reaches a plateau, i.e., the field dependence of paramagnetic relaxation is saturated.)

SOC is usually invoked as an interaction responsible for the "leakage" of magnetic and spin effects. In such cases SOC is basically considered as a fitting parameter, namely MF-independent first-order rate constant of ISC k_{SOC}. At the same time the role of SOC not as an interaction triggering ISC, but as enhancing paramagnetic relaxation, should be considered.

We will consider (Schemes VI and VII) the most general approach to ISC in RP (IRP, biradical) in order to understand the role and place of SOC-induced transitions. The generic scheme of ISC's in the absence or in the presence of external MF should be considered first (Scheme VI). A more detailed consideration (Scheme VII) includes the internal conversion (IC) between triplet sublevels in a magnetic field and different possible interactions, which induce transitions according to different mechanisms among these sublevels and between them and the singlet state.

It is desirable to have answers to the following questions for understanding of MFE in triplet RP's (Schemes VI and VII): (i) Which is the rate-limiting step? (IC or ISC?) (ii) At what structure of the RP (IRP, biradical) does the rate-determining step occur? (Contact or spatially separated RP or both, compact or elongated biradical or both?) (iii) What magnetic interaction triggers ISC and IC (SOC, Δg, HFC, etc.)? (iv) Is the interaction static (like HFC) or modulated (like SOC)? (v) Is the rate-limiting step, if modulated, limited by spectral density (resonance motion of the "bath"), or energy accepting (phonon "bottleneck" in the ability of the "bath" to accept energy)?

Scheme VIII



The possible interactions and relaxation channels capable of triggering both intersystem crossing (ISC) and internal conversion (IC) are summarized in the Table VI. Being restricted with our specific topic, we will not present the complete analysis of experimental data on MFE's. A useful classification of MFE's and ways or their discrimination based on field dependencies (A vs B) is presented in ref 3. The criteria for existence of SOC-induced transitions are presented above. It is worthwhole to note that under consideration of quenching action of SOC, it is desirable to compare T_1 of free radicals "with strong SOC action" and "without strong SOC action", and to try to estimate whether "leak" in MFE can be ascribed simply to decrease of T_1.

The description of MFE can be done within the framework of a structural model. The structural model of RP (IRP, biradical), which consists of two states: contact RP (IRP, exciplex, stiff biradical) and well-separated RP (IRP, elongated biradical), section 2.3, Figure 3. The former state is characterized by large exchange interactions $|J| \gg A_{eff}$, and the latter state, by negligible or zero exchange interaction $J \approx 0$. Depending upon the presence (or absence) of external MF and J value (or configuration of RP or IRP or biradical) one may consider four situations (Scheme VIII).

The curved lines on Scheme VIII stand for ISC between different triplet sublevels and the singlet state.

The SOC in pairs of light radicals (or C-centered biradicals) is usually considered to decay exponentially with the distance R between radical fragments.[180] At the same time in the case when a partner of RP (or a biradical terminus) has a strong SOC, (i.e., being metal-centered radical or possessing nonquenched angular momentum), the SOC of RP is determined by this partner and does not strongly depend upon R and can be operative even in spatially-separated RP's (see section 4.4).

The Schemes VI–VIII and considerations presented above hopefully will help an experimentalist to understand the nature of observed MFE, to determine whether SOC is an important factor in one or more of the steps involved in the MFE process and to design critical and revealing experiments concerning these issues.

7. Conclusions and Perspectives

In this review article we have considered the manifestation of SOC in the elementary acts of formation and decay of exciplexes, radical pairs, biradicals, and other intermediates of importance to photochemistry. The major conclusions are that the *SOC acts in two ways*, one promoting MFE and the other quenching MFE, and that SOC promotes MFE through two major mechanisms (TM and Δg) and quenches MFE creating a general sink for the spin coherency in a system.

Among the most important parameters of photochemical intermediates is the efficiency of cage reaction or its "inverse", i.e., the efficiency of cage escape, **e**. Factors influencing the efficiency of escape of photogenerated *geminate* radical pairs from a solvent cage (or the cage provided by a restricted reaction space) are very important both for the theoretical investigation and practical application of photochemistry. In this review article we have shown convincing examples that SOC can be an important factor in determining the efficiency of cage effects, and through the agency of the cage effect, that SOC can be an important factor in determining the magnitude and direction of MFE and the dependence of MFE on the variation of magnetic flux density of applied field.

The observation of MFE's induced by the triplet mechanism is expected to be rare and only when a very narrow set of experimental parameters are met. These parameters characterize the process of spin relaxation ($1/T_1$), spin-selective interconversion ($|D_k|$), and the dissociation rate (k_d) of the triplet intermediate. The observation of TM requires that the following inequality is valid:

$$|D_k| \gg 1/T_1, k_d \tag{72}$$

If the inequality 72 inverts sign and inequality 73 holds true one should expect that neither the triplet, nor HFC

$$1/T_1 \gg |D_k|, k_d, \tag{73}$$

and Δg mechanisms of MFEs will work; in other words, the reaction will not be magnetosensitive. In such a case triplet sublevels lose their individually, and SOC provides a mechanism for rapid T–S interconversion, which restores the spin equilibrium in the RP faster than any spin-selective processes required for MFE.

The extreme situations described by eqs 72 and 73 are rather rare. (The trivial exception would be a photostable molecule at liquid helium temperatures.) Although the observation of TM has been reported for a very narrow class of liquid-phase reactions, there are much more examples related to the Δg mechanism, where SOC also induces MFE's through its effect on the difference in g factors of the radicals in a pair. However, despite the fact that the increase in SOC for these systems usually results in a Δg increase, the number of such examples in which the Δg mechanism is important is reduced for compounds possessing heavy atoms. The point is that SOC simultaneously leads to an acceleration of SLR in free radicals and intermediates due to spin rotational and/or Kronig–Van Vleck–Orbach mechanisms. In addition, if the solvent contains a high concentration of heavy atoms, an additional channel for SLR is opened.

Finally, when $1/T_1 \gg |D_k|$, the heavy atom-stimulated T–S interconversion in contact RP's, triplet exciplexes, and biradicals is another important source of the SOC-induced quenching of MFEs.

In spite of the inherent "quenching" ability of SOC, MFE's, and even in certain cases MIE's, have been observed in reactions involving sulfur-, germanium-, phosphorus-, tin-, ruthenium-, cobalt-, magnesium-, mercury-, manganese-, silicon-, copper-, uranium-centered organoelemental and inorganic radicals. Although the observed effects are relatively small, their existence demonstrates the possibility of magnetosensitive coherent transitions in systems containing heavy atoms. It would be informative to search for CIDNP involving magnetic nuclei of some elements in heavy atom-centered radicals mentioned above, e.g. ^{73}Ge, ^{99}Ru, ^{101}Ru, or ^{235}U.

At present MIE has been found for relatively few "heavy elements" (^{17}O, ^{29}Si, ^{33}S, and ^{235}U); see Table V.[213] It is possible that the MIE-based processes of isotope separation might be useful in practice. It is expected that magnetic isotope separation will be more efficient than mass isotope separation.[169] An understanding of the nature of the competing HFC and SOC interactions is absolute crucial in maximizing the efficiency of the MIE in radical pairs containing heavy atoms.

Interesting issues which arise from the literature reviewed in this report are the understanding and control of the role that spin–orbit coupling plays in the spin dynamics of radical pair, exciplexes, biradicals, etc. Many examples have been presented in this report, for which SOC does not significantly manifest itself in magnetic and spin effects in radical reactions despite the presence of a heavy atom in one of the partners of the pair. Thus, the question arises why the presence of a heavy atom does not the guarantee a significant effect of SOC on the spin dynamics of a system. The *first* and trivial reason for the absence of a SOC effect occurs when the heavy atom is remote from the reaction center, and/or the spin density on this atom is absent. The *second* possible reason is that the heavy atom has an electronic configuration such that its valence shell electrons are screened from the electric field of the nucleus. The *third* reason is that the radical has an electronic configuration such that its orbital momentum is strongly suppressed. The latter may be due to a symmetry feature ($\Lambda = 0$ for linear radicals) or to an energetic feature ($\Delta \gg \xi$).

The possibility of manipulating and controlling the effectiveness of SOC by controlling the orbital configuration is the most interesting in practice, because it opens up the possibility for significant SOC variation in the system by the variation of the structure of a compound containing a certain heavy atom. This manipulation can proceed by considering the anisotropy of the *g* factor and the value of spin–orbit-induced fine splitting in complexes of paramagnetic ions, which may serve as the experimental criteria which enable one to estimate the magnitude of SOC in a system.

Further theoretical and experimental work is necessary for elucidation of optimal conditions for observation of MFE's involving radical reactions involving reagents containing heavy atoms. The effects of solvent viscosity, microenvironment, and polarity[259] in such reactions should be examined in these analyses.

The investigation of SOC in spatially well-separated RP's is of particular interest. The data on different magnetic and spin effects in free-radical reactions proceeding via heteroatom- and metal-centered free radicals is isolated and scattered. (Most of research was made by ^{1}H CIDNP technique, cf. Table V.) It would be instructive to make a judicious choice of specific (photo)chemical reactions and to identify most of the important parameters with the aid of different experimental techniques (ESR spectra of heteroatom- or metal-centered free radicals and paramagnetic relaxation times, cage effects and rate constants of elementary reaction steps, magnetic field effects, CIDEP and CIDNP spectra, etc). The important observations would be CIDNP and CIDEP in reactions involving heteroatom- and metal-center radicals.

Acknowledgments. N.J.T. and I.V.K. thank the NSF, DOE and AFOSR for their generous support of this research. Yu.A.S. is grateful to the Alexander von Humboldt Foundation for the financial support which made it possible for him to work in Prof. U. E. Steiner's research group at the University of Konstanz. The authors are indebted to Prof. U. E. Steiner for many useful comments to the draft version of the manuscript; a number of theoretical issues described in this review article (sections 2.2, 2.3, 3.1, 3.2, and 4.1) were written under the strong influence of scientific collaboration and numerous stimulating discussions with Prof. U. E. Steiner.

8. List of Abbreviations and Definitions

AO	atomic orbital
CIDEP	chemically-induced dynamic electron polarization
CIDNP	chemically-induced dynamic nuclear polarization
EHA	external heavy atom
HFC	hyperfine coupling
IC	internal conversion
IHA	internal heavy atom
IRP	ion–radical pair
IRSOC	intraradical spin–orbit coupling
ISC	intersystem crossing
FT	Fourier transform
MF	magnetic field
MFE	magnetic field effect
MIE	magnetic isotope effect
MO	molecular orbital
RP	radical pair
SDS	sodium dodecyl sulfate
SLE	stochastic Liouville equation
SLR	spin–lattice relaxation
SNP	stimulated nuclear polarization
SOC	spin–orbit coupling
SRR	spin–rotational relaxation
TM	triplet mechanism
TR	time resolved
ZFS	zero-field splitting
$\mathcal{A}$	electron acceptor
$\mathbf{A}$	tensor of hyperfine interaction in free radical
A_{eff}	effective HFC coupling constant of RP or biradical
$\delta A = A_{\perp} - A_{\parallel}$	difference between the principal values of A tensor
ΔA	anisotropy of magnetic field effect due to photoexcitation with polarized light
$\mathbf{B}$, B	magnetic field flux density (vector and scalar)
$\mathcal{D}$, $\mathcal{D}$	electron donor
D and E	ZFS parameters of a triplet state
D_k and E_k	parameters of SOC-induced sublevel selective T $\rightarrow$ S interconversion
D_{R}	coefficient of rotational diffusion
e	value of escape of radicals from a cage

E	stands for chemical element heavier than oxygen
$\mathbf{e}_0$	value of escape of radicals from a cage in the Earth's magnetic field
$\mathbf{e}_B$	value of escape of radicals from a cage in the presence of an external magnetic field of flux $\boldsymbol{B}$
$\mathbf{g}$	tensor of a free radical
g_e	g factor of free electron
g_s	isotropic part of $\mathbf{g}$ tensor
Δg	difference in g factors of two free radicals
$\delta g = g_{\perp} - g_{\parallel}$	difference between the principal values of $\mathbf{g}$ tensor
$\mathbf{I}$	nuclear spin
I	moment inertia of a radical
$I_Z = M_I$	nuclear magnetic quantum number
J	exchange interaction energy
J	total electronic quantum number
$\mathbf{J}$	total electronic angular momentum
k_B	the Boltzmann constant
k_d, s^{-1}	rate constant of dissociation of an exciplex or an RP or IRP, when the processes are considered as a first-order reaction
k_{diff}, M^{-1} s^{-1}	diffusion rate constant for a random encounter of reagents in a solvent bulk
k_{HFC}, s^{-1}	rate constant of ISC induced by HFC in RP or biradical, when the process is considered as a first-order reaction
k_{obs}, s^{-1}	rate constant of a RP or biradical decay, when the process is considered as a first-order reaction
k_r, s^{-1}	rate constant of a formation of chemical product(s) as a result of RP or biradical decay, when the process is considered as a first-order reaction
k_{rel}, s^{-1}	rate constant of paramagnetic relaxation
k_{SOC}, s^{-1}	rate constant of T → S interconversion induced by SOC in RP or biradical, when the process is considered as a first-order reaction
ℓ	orbital quantum number
ℓ_i	orbital angular momentum of the i-th electron
L	total electronic orbital angular momentum quantum number
$\mathbf{L}$	total electronic orbital angular momentum
$\mathbf{L}_Z$	z component of electronic orbital angular momentum
M_I	see I_Z above
n	principal quantum number
P	enhancement factor in CIDEP spectra
ΔP	anisotropy of enhancement factor in CIDEP spectra due to photoexcitation with polarized light
r	hydrodynamic radius of a particle
R	distance between radical centers in a RP or biradical
S	spin quantum number
$\mathbf{S}$	total spin angular momentum of many-electron system
$\mathbf{S}_Z$	z component of spin angular momentum
$\mathbf{s}_i$	spin angular momentum on the i-th electron in an atom
T_1	longitudinal electronic relaxation time in free radicals
T_2	transverse electronic relaxation time in free radicals
T_{1n}	longitudinal nuclear relaxation time in a diamagnetic molecule
${T_{1n}}^R$	longitudinal nuclear relaxation time in free radical
V	enhancement factor in CIDNP spectra
W_{ij}	rate constant of spin–lattice relaxation between triplet sublevels i and j
z	axis of symmetry in (diatomic) molecule
Z	nuclear charge of an atom, atomic number
Z_{en}, s^{-1}	frequency of encounters of molecules of two different compounds in a liquid
A	magnetic field effect
β_e	Bohr magneton for electron
Δ	energy gap between the ground electronic level and the closest excited state of different orbital symmetry
Δ_c	decrease of exchange integral in a RP or biradical decay with distance
η	dynamic solvent viscosity
Λ	projection of the electronic orbital angular momentum in diatomic molecule on the molecular axes
ξ	effective SOC constant for polyatomic system
ξ_A	effective SOC constant for the valence shell electrons of atom A
ξ_h	effective SOC constant for polyatomic radical
$\xi_{n\ell}$	SOC constant for a specific $n\ell$ state of the atom
ρ	reaction radius, i.e. sum of van der Waal radii of reagents
ρ_A	spin density on an atom A
σ	spin statistical factor in bimolecular reaction
Σ	projection of the electronic spin angular momentum in diatomic molecule on its axes
τ	lifetime of a triplet state
τ_J	rotational angular momentum relaxation time
$\tau_{\theta 2}$	orientational relaxation time of second-rank tensor
ϕ	interatomic electric field potential
Ω	projection of the total electronic angular momentum in diatomic molecule on the molecular axes
ω_0	Larmor frequency of an electron

9. References

(1) Salikhov, K. M.; Molin, Yu. N.; Sagdeev, R. Z.; Buchachenko, A. L. *Spin Polarization and Magnetic Effects in Radical Reactions*; Elsevier: Amsterdam, 1984.

(2) Turro, N. J. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 609.

(3) (a) Hayashi, H.; Sakaguchi, Y. In *Lasers in Polymer Science and Technology: Applications*; Fouassier, J.-P., Rabek, J. F., Eds.; CRC Press, Boca Raton, 1990; Vol. 2, p 1. (b) Hayashi, H. In *Photochemistry and Photophysics*; Rabek, J. F., Ed.; CRC Press, 1990; Vol. 1, Chapter 2, p 59.

(4) Steiner, U. E.; Ulrich, T. *Chem. Rev.* **1989**, *89*, 51.

(5) Steiner, U. E.; Wolff, H.-J. In *Photochemistry and Photophysics*; Rabek, J. F., Ed.; CRC Press: Boca Raton, 1991; Vol. IV, Chapter 1, p 1.

(6) Zeldovich, Ya. B.; Buchachenko, A. L.; Frankevitch, E. L. *Uspekhi Fiz. Nauk* **1988**, *155*, 3.

(7) McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice-Hall: Engelwood Cliffs, 1969.

(8) Weltner, W. *Magnetic Atoms and Molecules*, Van Nostrand: New York, 1983.

(9) Barltrop, J. A.; Coyle, J. D. *Excited States in Organic Chemistry*; Wiley: London, 1975.

(10) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, 1978.

(11) Horie, H. *Progr. Theor. Phys.* (*Kyoto*), **1953**, *10*, 296.

(12) (a) Richards, W. G.; Trivedi, H. P.; Cooper, D. L. *Spin-Orbit Coupling in Molecules*; Oxford University Press: Oxford, 1981. (b) Moore, C. E. *Atomic Energy Levels*, Circular No. 467; National Bureau of Standards: Washington, DC, 1958; Vols. 1–3.

(13) (a) Dagdigian, P. J.; Campbell, M. L. *Chem. Rev.* **1987**, *87*, 1. (b) Dagdigian, P. J. In *Selectivity in Chemical Reactions*; Whitehead, J. C., Ed.; Kluwer Academic: Dordrecht, 1988; p 147.

(14) Kohlmann, S.; Kasack, V.; Roth, E.; Kaim, W. *J. Chem. Soc. Faraday Trans.* **1989**, *1*, 85; 4047.

(15) Atkins, P. W. *Quanta. A Handbook of Concepts*; Clarendon Press: Oxford, 1974.

(16) Griffith, J. S. *The Theory of Transition Metal Ions*; Cambridge University Press: London, 1964.

(17) Fordyce, W. A.; Brummer, J. G.; Crosby, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 7061.

(18) (a) Denning, R. G.; Snellgrove, T. R.; Woodwark, D. R. *Mol. Phys.* **1979**, *37*, 1109. (b) Lefebvre-Bion, H.; Field, R. W. *Perturbations in the Spectra of Diatomic Molecules*; Academic: Orlando, 1986.

(19) Van Vleck, J. H. *Rev. Modern Phys.* **1951**, *23*, 213.

(20) (a) Herzberg, G. *Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules*, Van Nostrand: Princeton, 1950. (b) Herzberg, G. *The Spectra and Structures of Simple Free Radicals. An Introduction to Molecular Spectroscopy*; Cornell University Press: Ithaca, 1971.

(21) Muldahmetov, Z. M.; Minaev, B. F.; Ketzle, G. A. *Optical and Magnetic Properties of the Triplet State*; Nauka Publishers: Alma-Ata, Kazakhstan, 1983 (in Russian).

(22) Minaev, B. F.; Muldakhmetov, Z. M.; Irgibaeva, I. S.; Tlepbergenov, T. O.; Kizhner, D. I. *Int. J. Quant. Chem.* **1982**, *22*, 863.
(23) Klotz, R.; Marian, C. M.; Peyerimhoff, S. D.; Hess, B. A.; Buenker, R. J. *Chem. Phys.* **1984**, *89*, 223.
(24) Marian, C. M.; Klotz, R. *Chem. Phys.* **1985**, *95*, 213.
(25) Klotz, R.; Peyerimhoff, S. D. *Mol. Phys.* **1986**, *57*, 573.
(26) Matsushita, T.; Klotz, R.; Marian, C.; Peyerimhoff, S. *Mol. Phys.* **1987**, *62*, 1385.
(27) Thümmel, H.; Klotz, R.; Peyerimhoff, S. D. *Chem. Phys.* **1989**, *135*, 229.
(28) Henry, B. R.; Siebrand, W. *Chem. Phys. Lett. 3*, **1969**, *90*, 728.
(29) Metz, F.; Friedrich, S.; Hohlneicher, G. *Chem. Phys. Lett.* **1972**, *16*, 353.
(30) Langhoff, S. R. *J. Chem. Phys.* **1980**, *73*, 2379.
(31) Cohen, J. S.; Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1979**, *71*, 2955.
(32) Koziar, J. C.; Cowan, D. O. *Acc. Chem. Res.* **1978**, *11*, 334.
(33) Buchachenko, A. L.; Wasserman, A. M. *Stable Radicals*; Khimia Publishers: Moscow, Russia, 1973 (in Russian).
(34) Minaev, B. F. *Z. Phys. Chem. N.F.*, in press.
(35) Sugano, S.; Tanabe, Y.; Kamimura, H. *Multiplets of Transition-Metal Ions in Crystals*; Academic: New York, 1970.
(36) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Clarendon Press: Oxford, 1970.
(37) Fischer, H., Helwege, K.-H., Eds. *Magnetic Properties of Free Radicals*; Springer: Berlin, 1977.
(38) Treinin, A.; Loeff, I.; Hurley, J. K.; Lunschitz, H. *Chem. Phys. Lett.* **1983**, *95*, 333.
(39) (a) DeSimone, R. E.; Drago, R. S. *J. Am. Chem. Soc.* **1970**, *92*, 2343. (b) Kobler, E. M.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1614.
(40) (a) Miyake, S.; Yamana, Y.; Imoto, S.; Ohiya-Nishiguchi, H. *Inorg. Chim. Acta* **1984**, *95*, 17. (b) Miyake, S.; Kondo, T.; Imoto, S.; Ohiya-Nishiguchi, H. *J. Less-Common Met.* **1986**, *122*, 313.
(41) Steiner, U. E.; Haas, W. *J. Phys. Chem.* **1991**, *95*, 1880.
(42) Harris, A. L.; Brown, J. K.; Harris, C. B. *Ann. Rev. Phys. Chem.* **1988**, *39*, 341.
(43) Sceats, M. G. *Chem. Phys.* **1985**, *96*, 299.
(44) Morita, A.; Kato, S. *J. Phys. Chem.* **1992**, *96*, 1067.
(45) Furlani, T. R.; King, H. F. *J. Chem. Phys.* **1985**, *82*, 5577.
(46) Carlacci, L.; Doubleday, C.; Furlani, T. R.; King, H. F.; McIver, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 5323.
(47) Hurley, J. K.; Linschitz, H.; Treinin, A. *J. Phys. Chem.* **1988**, *92*, 5151.
(48) Winter, G.; Shioyama, H.; Steiner, U. E. *Chem. Phys. Lett.* **1981**, *81*, 547.
(49) Steiner, U. E.; Wolff, H.-J.; Ulrich, T.; Ohno, T. *J. Phys. Chem.* **1989**, *93*, 5147.
(50) Steiner, U. E.; Bürssner, D. *Z. Phys. Chem. N.F.* **1990**, *169*, 159.
(51) Wolff, H.-J.; Steiner, U. E. *Z. Phys. Chem. N.F.* **1990**, *169*, 147.
(52) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.
(53) (a) Zimmt, M. B.; Doubleday, C.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6726. (b) Closs, G. L.; Redwine, O. D. *J. Am. Chem. Soc.* **1985**, *107*, 4543. (c) Closs, G. L.; Redwine, O. D. *J. Am. Chem. Soc.* **1985**, *107*, 6131.
(54) (a) Wong, S. K.; Hutchinson, D. A.; Wan, J. K. S. *J. Chem. Phys.* **1973**, *58*, 985. (b) Atkins, P. W.; McLauchlan, K. A. In *Chemically Induced Magnetic Polarization*; Lepley, A. R., Closs, G. L., Eds.; Wiley: New York, 1973; p 41.
(55) Buckley, C. D.; McLauchlan, K. A. *Mol. Phys.* **1985**, *54*, 1.
(56) McLauchlan, K. A.; Stevens, D. G. *Mol. Phys.* **1987**, *60*, 1159.
(57) Turro, N. J.; Khudyakov, I. V. *Chem. Phys. Lett.* **1992**, *193*, 546.
(58) Sukhenko, S. A.; Salikhov, K. M. *Chem. Phys.* **1985**, *100*, 253.
(59) Steiner, U. E. *Ber. Bunsen-Ges. Phys. Chem.* **1981**, *85*, 228.
(60) Ulrich, T.; Steiner, U. E.; Föll, R. E. *J. Phys. Chem.* **1983**, *87*, 1873.
(61) Levin, P. P.; Shafirovich, V. Ya.; Klimtchuk, E. S.; Kuzmin, V. A.; Mayer, V. E.; Yablonskaya, E. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, 1436.
(62) The polarization of a component in ESR spectrum or polarization of NMR signal of a molecule or of a group is measured in terms of enhancement factor (V), which is defined as follows: $V = (S - S_0)/S_0$, where S is the observed signal intensity (or height) and S_0 is what the would be if all the spin states were populated according to the Boltzmann distribution. We will use in the review V for enhancement factor in CIDNP and P for electron polarization in CIDEP.
(63) Atkins, P. W.; Evance, G. T. *Mol Phys.* **1974**, *27*, 1633.
(64) Pedersen, J. B.; Freed, J. H. *J. Chem. Phys.* **1975**, *62*, 1706.
(65) Atkins, P. W.; Topping, G. S. *Mol. Phys.* **1982**, *46*, 941.
(66) (a) Adrian, F. J. *J. Chem. Phys.* **1974**, *61*, 4875. (b) Adrian, F. J. *Rev. Chem. Intermed.* **1986**, *7*, 173.
(67) Serebrennikov, Yu. A.; Minaev, B. F.; Mukhin, R. R.; Muldakhmetov, Z. M. *Teor. Eksp. Khim.* **1986**, *22*, 203.
(68) Mukhin, R. R.; Serebrennkov, Yu. A.; Minaev, B. F.; Muldakhmetov, Z. M. *Teor. Eksp. Khim.* **1988**, *24*, 95.
(69) Serebrennkov, Yu. A.; Minaev, B. F. *Chem. Phys.* **1987**, *114*, 359.
(70) Serebrennikov, Yu. A.; Abdrakhmanov, B. M.; Minaev, B. F. *Khim. Fiz.* **1987**, *6*, 799.
(71) Serebrennikov, Yu. A.; Mukhin, R. R. Minaev, B. F. *Russ. J. Phys. Chem.* **1989**, *63*, 395.
(72) Burshtein, A. I.; Temkin, S. I. *Spectroscopy of the Molecular Rotation in Gases and Liquids*; Nauka Publishers: Novosibirsk, Russia, 1982 (in Russian).
(73) Sixl, H.; Schwoerer, M. *Chem. Phys.* **1970**, *6*, 21.
(74) Dellinger, B.; Hochstrasser, R. M.; Smith, A. B., III. *J. Am. Chem. Soc.* **1977**, *99*, 5834.
(75) Gorter de Vries, H.; Hoff, A. J. *Chem. Phys. Lett.* **1978**, *55*, 395.
(76) Clarke, R. H.; Connors, R. E.; Keegan, J. *J. Chem. Phys.* **1977**, *66*, 358.
(77) Gehrtz, C.; Bräuchle, C.; Voitländer, J. *Z. Naturforsh.* **1981**, *36a*, 743.
(78) Freed, J. H. In *Electron Spin Relaxation in Liquids*; Muus, L. T., Atkins, P. W., Eds.; Plenum: New York, 1972; p 503.
(79) Burshtein, A. I. *Lectures on Quantum Kinetics*; Novosibirsk University Publishers: Novosibirsk, Russia, 1968 (in Russian).
(80) Alexandrov, I. V. *The Theory of Magnetic Relaxation*; Nauka Publishers: Moscow, Russia, 1975 (in Russian).
(81) Dobbs, A. J.; McLauchlan, K. A. *Chem. Phys. Lett.* **1975**, *30*, 257.
(82) Adeleke, B. B.; Choo, K. Y.; Wan, J. K. S. *J. Chem. Phys.* **1975**, *62*, 3822.
(83) Roth, H. D.; Schilling, M. L. M.; Hutton, R. S. *J. Chem. Phys.* **1979**, *71*, 610.
(84) Yamauchi, S.; Tominaga, K.; Hirota, N. *J. Phys. Chem.* **1986**, *90*, 2367.
(85) It is probable that in the first publications (refs 81 and 82) the systematic measurement error has been done; later on this error has received attention (ref 83).
(86) Regev, A.; Michaeli, S.; Levanon, H.; Cyr, M.; Sessler, J. L. *J. Phys. Chem.* **1991**, *95*, 9121.
(87) (a) Boxer, S. G.; Chidsey, C. E. D.; Roelofs, M. G. *J. Am. Chem. Soc.* **1982**, *104*, 2674. (b) Boxer, S. G.; Chidsey, C. E. D.; Roelofs, M. G. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 4632.
(88) Gerstman, B. S.; Austin, R. H.; Hopfield, J. J. *Phys. Rev. Lett.* **1981**, *47*, 1636.
(89) Redi, M. H.; Gerstman, B. S.; Hopfield, J. J. *Biophys. J.* **1981**, *35*, 471.
(90) Doetschman, D. C.; Szumowski, J. *J. Chem. Phys.* **1986**, *84*, 2866.
(91) (a) Stone, A. J. *Proc. R. Soc.* **1963**, *A271*, 424. (b) Stone, A. J. *Mol. Phys.* **1963**, *6*, 509.
(92) Klimtchuk, E. S.; Khudyakov, I. V.; Serebrennikov, Yu. A. *Zhurn. Fiz. Khim.* **1990**, *64*, 2833.
(93) Molin, Yu. N.; Sagdeev, R. Z.; Leshina, T. V.; Podoplelov, A. V.; Dushkin, A. V.; Grishin, Yu. A.; Weiner, L. M. In *Magnetic Resonance and Related Phenomena*; Kundla, E., Lippmaa, E., Saluvere, T., Eds.; Springer: Berlin, 1979; p 49.
(94) Vanag, V. K.; Kuznetzov, A. N.; Pyruzyan, L. A. *Biofizika* **1983**, *28*, 18.
(95) Horvath, A.; Zsilak, Z.; Papp, S. *J. Photochem. Photobiol.* **1989**, *A50*, 129.
(96) Van Vleck, J. H. *Phys. Rev.* **1932**, *40*, 544.
(97) Minaev, B. *Opt. Spectrosk.* **1978**, *44*, 148 (in Russian).
(98) Atkins, P. W.; Stannard, P. R. *Chem. Phys. Lett.* **1977**, *47*, 113.
(99) Stannard, P. R. *J. Chem. Phys.* **1978**, *68*, 3932.
(100) Ferraudi, G.; Pacheco, M. *Chem. Phys. Lett.* **1984**, *112*, 187.
(101) Ferraudi, G.; Argüello, G. A.; Frink, M. E. *J. Phys. Chem.* **1987**, *91*, 64.
(102) Ronco, S.; Ferraudi, G. *Inorg. Chem.* **1990**, *29*, 3961.
(103) Ferraudi, G.; Argüello, G. A. *J. Phys. Chem.* **1988**, *92*, 1846.
(104) Ronco, S.; Perkovic, M.; Ferraudi, G.; Gozzi, M. *Chem. Phys.* **1992**, *162*, 95.
(105) Carrington, A.; McLachlan, A. D. *Introduction to Magnetic Resonance*; Chapman and Hall: London, 1979.
(106) Altshuler, S. A.; Kozirev, B. M. *Electron Paramagnetic Resonance in Compounds of Transition Elements*; Wiley: Jerusalem, 1974.
(107) Atkins, P. W.; Kivelson, D. *J. Chem. Phys.* **1966**, *44*, 169.
(108) Hubbard, P. S. *Phys. Rev.* **1963**, *131*, 1155.
(109) McLauchlan, K. A.; Sealy, R. C.; Wittmann, J. M. *Mol. Phys.* **1978**, *36*, 1397.
(110) Prabhananda, B. S.; Hyde, J. S. *J. Chem. Phys.* **1986**, *85*, 6705.
(111) Hayashi, H.; Sakaguchi, Y.; Kamachi, M.; Schnabel, W. *J. Phys. Chem.* **1987**, *91*, 3936.
(112) Ulrich, T.; Steiner, U. E.; Schlenker, W. *Tetrahedron* **1986**, *42*, 6131.
(113) Levin, P. P.; Kuzmin, V. A. *Chem. Phys. Lett.* **1990**, *165*, 302.
(114) Levin, P. P.; Kuzmin, V. A.; Khudyakov, I. V. *Khim. Fiz.* **1989**, *8*, 902.
(115) Hayashi, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 322.
(116) Steiner, U. E.; Wu, J. Q. *Chem. Phys.* **1992**, *162*, 53.
(117) Baumann, D. Ph.D. Thesis, Universität Konstanz, in preparation.
(118) Wu, J. Q.; Steiner, U. E.; Baumann, D. *Z. Phys. Chem. N.F.*, in press.
(119) Turro, N. J.; Weed, G. C. *J. Am. Chem. Soc.* **1983**, *105*, 1861.
(120) Ulrich, T.; Steiner, U. E. *Chem. Phys. Lett.* **1984**, *112*, 365.
(121) de L. Kronig, R. *Physica* **1939**, *6*, 33.
(122) (a) Van Vleck, J. H. *J. Chem. Phys.* **1939**, *7*, 72. (b) Van Vleck, J. H. *Phys. Rev.* **1940**, *57*, 426.
(123) Kivelson, D. *J. Chem. Phys.* **1966**, *45*, 1324.
(124) Bloembergen, N.; Morgan, L. O. *J. Chem. Phys.* **1961**, *34*, 842.
(125) Rubinstein, M.; Baram, A.; Luz, Z. *Mol. Phys.* **1971**, *20*, 67.

(126) Friedman, H. L.; Holz, M.; Hertz, H. G. *J. Chem. Phys.* **1979**, *70*, 3369.
(127) Orbach, R. *Proc. Phys. Soc., London* **1961**, *A77*, 821.
(128) Kowalewski, J.; Nordenskiöld, L.; Benetis, N.; Westlund, P.-O. *Prog. NMR Spectrosc.* **1985**, *17*, 141.
(129) Blanci, L.; Bertini, I.; Luchinat, C. *Nuclear and Electron Relaxation*; VCH Publishers: Weinheim, 1991.
(130) Serebrennikov, Yu. A.; Steiner, U. E. *Z. Phys. Chem. N.F.*, in press.
(131) Leung, A. F.; Wong, E. Y. *Phys. Rev.* **1969**, *180*, 380.
(132) (a) Sandhu, S. S.; Sidhu, M. S.; Singh, R. J. *J. Photochem. Photobiol.* **1987**, *39*, 229. (b) Sandhu, S. S.; Sidhu, M. S.; Singh, R. J. *J. Photochem. Photobiol.* **1989**, *A46*, 213.
(133) Gordeev, E. P.; Nikitin, E. E.; Ovchinnikova, M. Ya. *Can. J. Phys.* **1969**, *47*, 819.
(134) Minaev, B. F.; Danilovich, I. M.; Serebrennikov, Yu. A. In *Dynamics of Triplet Excitations in the Molecular Crystals*; Davydov, A. S., Ed.; Naukova Dumka Publishers: Kiev, Ukraine, 1989; p 109 (in Russian).
(135) (a) Klimtchuk, E. S.; Makarov, B. P.; Serebrennikov, Yu. A.; Khudyakov, I. V. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1989**, 1627. (b) Klimtchuk, E. S.; Irinyi, G.; Khudyakov, I. V.; Marguilis, L. A.; Kuzmin, V. A. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 4119. (c) Klimtchuk, E. S. Ph.D. Thesis, Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka, 1990.
(136) Turro, N. J.; Lei, X.; Gould, I. R.; Zimmt, M. B. *Chem. Phys. Lett.* **1985**, *120*, 397.
(137) Sakaguchi, Y.; Hayashi, H. *Chem. Phys. Lett.* **1984**, *106*, 420.
(138) Shkrob, I. A.; Margulis, L. A.; Tarasov, V. F. *Zhurn. Fiz. Khim.* **1989**, *63*, 3338.
(139) Uehata, A.; Nakamura, H.; Usui, S.; Matsuo, T. *J. Phys. Chem.* **1989**, *93*, 8197.
(140) Wang, J.; Welsh, K. M.; Waterman, K. C.; Fehlner, P.; Doubleday, C.; Turro, N. J. *J. Phys. Chem.* **1988**, *92*, 3730.
(141) Basu, S.; Nath, D.; Chowdhury, M. *J. Lumin.* **1988**, *40/41*, 252.
(142) Basu, S.; Kundu, L.; Chowdhury, M. *Chem. Phys. Lett.* **1987**, *141*, 115.
(143) Tanymoto, Y.; Kita, A.; Itoh, M.; Okazaki, M.; Nakagaki, R.; Nagakura, S. *Chem. Phys. Lett.* **1990**, *165*, 184.
(144) Sakaguchi, Y.; Hayashi, H. *Chem. Phys.* **1992**, *162*, 119.
(145) Shafirovich, V. Ya.; Batova, E. E.; Levin, P. P. *Chem. Phys. Lett.* **1990**, *172*, 10.
(146) Levin, P. P.; Kuzmin, V. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, 298.
(147) Levin, P. P. D.Sc. Thesis, Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia, 1990.
(148) Turro, N. J.; Zimmt, M. B.; Lei, X. G.; Gould, I. R.; Nitsche, K. S.; Cha, Y. *J. Phys. Chem.* **1987**, *91*, 4544.
(149) Benn, R. *Rev. Chem. Intermed.* **1979**, *3*, 45.
(150) Kaptein, R. *J. Am. Chem. Soc.* **1972**, *94*, 6251.
(151) For RP's in viscous solutions and for those possessing magnetic nuclei with large HFC constants intersystem crossing according $S-T_-$ mechanism can occur (ref 152). This mechanism of ISC includes both HFC-dependent and HFC-independent contributions; see for discussion ref 152.
(152) McLauchlan, K. A. In *Lasers in Polymer Science and Technology: Applications*; Fouassier, J.-P.; Rabek, J. F., Eds.; CRC Press: Boca Raton, 1990, Vol. 1, p 259.
(153) Yankelevitch, A. Z.; Khudyakov, I. V.; Levin, P. P.; Serebrennikov, Yu. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 25.
(154) Turro, N. J.; Chung, C.-J.; Jones, G., II; Becker, W. G. *J. Phys. Chem.* **1982**, *86*, 3677.
(155) Yankelevitch, A. Z.; Khudyakov, I. V.; Buchachenko, A. L. *Khim. Fiz.* **1988**, *7*, 734.
(156) (a) Buchachenko, A. L.; Khudyakov, I. V. *Acc. Chem. Res.* **1991**, *24*, 177. (b) Buchachenko, A. L.; Khudyakov, I. V. *Russ. Chem. Rev.* **1991**, *60*, 555.
(157) Levin, P. P.; Khudyakov, I. V.; Kuzmin, V. A. *J. Phys. Chem.* **1989**, *93*, 208.
(158) Here and below any cage reaction between free radicals, viz. combination, disproportionation, or electron transfer, will be termed recombination for convenience.
(159) A pair of radical–ions $[\mathcal{A}^{\bullet -}, \mathcal{D}H^{\bullet +}]$ may be formed in electron-transfer reactions; it may also be formed in a hydrogen-abstraction reaction, when proton transfer follows the hydrogen-atom transfer: $[\mathcal{A}H^{\bullet}, \mathcal{D}^{\bullet}] \rightarrow [\mathcal{A}^{\bullet -}, \mathcal{D}H^{\bullet +}]$).
(160) Das, P. K.; Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4154.
(161) Hoshi, M.; Kikuchi, K.; Kokubun, M. *J. Photochem. Photobiol.* **1987**, *A41*, 53.
(162) Steiner, U. E.; Winter, G. *Chem. Phys. Lett.* **1978**, *55*, 364.
(163) Kikuchi, K.; Hoshi, M.; Abe, E.; Kokubun, H. *J. Photochem. Photobiol.* **1988**, *A45*, 1.
(164) According to ref 163 the SOC-induced ISC in a triplet RP determines back-electron transfer (recombination).
(165) Zakharova, G. V.; Chibisov, A. K. *Khim. Fiz.* **1990**, *9*, 1311.
(166) Olmsted, J., III; Meyer, T. J. *J. Phys. Chem.* **1987**, *91*, 1649.
(167) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.
(168) Braun, A. M. In *Photochemical Conversion and Storage of Solar Energy*; Pelizzetti, E., Schiavello, M., Eds.; Kluwer: Dordrecht, 1991; p 551.
(169) Wakasa, M.; Sakaguchi, Y.; Hayashi, H. *Chem. Phys. Lett.* **1991**, *176*, 541.
(170) Hayashi, H.; Sakaguchi, Y.; Mochida, K. *Chem. Lett.* **1984**, 79.
(171) Evance, C.; Ingold, K. U.; Scaiano, J. C. *J. Phys. Chem.* **1988**, *92*, 1257.
(172) Scaiano, J. C.; Abuin, E. B.; Stewart, L. C. *J. Am. Chem. Soc.* **1982**, *104*, 5673.
(173) Bohne, C.; Alnajjar, M. S.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 1444.
(174) Baglioni, P.; Ottaviani, M. F.; Martini, G. *J. Phys. Chem.* **1986**, *90*, 5878.
(175) Hayashi, H.; Sakaguchi, Y.; Tsunooka, M.; Yanagi, H.; Tanaka, M. *Chem. Phys. Lett.* **1987**, *136*, 436.
(176) Step, E. N.; Buchachenko, A. L.; Turro, N. J. *Chem. Phys.* **1992**, *162*, 189.
(177) Broomhead, E. J.; McLauchlan, K. A. *J. Chem. Soc., Faraday Trans. 2*, **1978**, *74*, 775.
(178) Levin, P. P.; Kuzmin, V. A. *Chem. Phys.* **1992**, *162*, 79.
(179) A_{eff} is the effective HFC constant of RP, which determines the rate of ISC (refs 1 and 2). $A_{\mathrm{eff}} = [\sum A_n^2 \mathrm{I}_n(\mathrm{I}_n + 1)]^{1/2}$, where A_n is the HFC constant of the n-th atom with a magnetic nucleus with spin I_n; summation is taken over all magnetic nuclei in both radicals (refs 1 and 4).
(180) Doubleday, C.; Turro, N. J.; Wang, J.-F. *Acc. Chem. Res.* **1989**, *22*, 199.
(181) Zimmt, M. B.; Doubleday, C.; Gould, I. R.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6724.
(182) Wang, J.-F. Ph.D. Thesis, Columbia University, New York, NY, 1990.
(183) Zimmt, M. B.; Doubleday, C.; Turro, N. J. *Chem. Phys. Lett.* **1987**, *134*, 549.
(184) Closs, G. L.; Forbes, M. D. E.; Piotrowiak, P. *J. Am Chem. Soc.* **1992**, *114*, 3285.
(185) Tanimoto, Y.; Takashima, M.; Hasegawa, K.; Itoh, M. *Chem. Phys. Lett.* **1987**, *137*, 330.
(186) Kikuchi, K.; Hoshi, M.; Niwa, T.; Takahashi, Y.; Miyashi, T. *J. Phys. Chem.* **1991**, *95*, 38.
(187) Perito, R. P.; Corden, B. B. *J. Am. Chem. Soc.* **1987**, *109*, 4418.
(188) Perito, R. P.; Corden, B. B. *Inorg. Chem.* **1988**, *27*, 1276.
(189) Hughes, M. E.; Corden, B. B. *J. Am. Chem. Soc.* **1989**, *111*, 4110.
(190) (a) Shafirovich, V. Ya.; Batova, E. E.; Levin, P. P. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 935. (b) Shafirovich, V. Ya.; Batova, E. E.; Levin, P. P. *Chem. Phys.* **1992**, *162*, 155.
(191) Saltiel, J.; Atwater, B. W. *Adv. Photochem.* **1988**, *14*, 1.
(192) Burshtein, A. I.; Khudyakov, I. V.; Yakobson, B. I. *Prog. React. Kinetics* **1984**, *13*, 221.
(193) Rüegge, D.; Fischer, H. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 3187.
(194) Meckstroth, W. K.; Walters, R. T.; Waltz, W. L.; Wojcicki, A.; Dorfman, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 1842.
(195) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187.
(196) Koroli, L. L.; Kuzmin, V. A.; Khudyakov, I. V. *Int. J. Chem. Kinet.* **1984**, *16*, 379.
(197) Khudyakov, I. V.; Nikulin, V. I.; Pisarenko, L. M. *Oxid. Communs.* **1988**, *11*, 181.
(198) (a) Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095. (b) For the sake of fairness it is also necessary to mention the value of $k_{59} = 1.8 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$ obtained earlier for the recombination of $(n\text{-}C_4H_9)Sn^{\bullet}$ in the same solvent at 295 K; see: Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 5399.
(199) Steiner, U. E.; Serebrennikov, Yu. A. Manuscript in preparation.
(200) Under organoelemental compounds we consider here those organic compounds, which contain elements *E* of the third period and beyond bonded to C. They include organometallic compounds and compounds containing Si, P, S, and Se. We will not consider halogen compounds here.
(201) Bangerter, B. W.; Beatty, R. P.; Kouba, J. K.; Wreford, S. S. *J. Org. Chem.* **1977**, *42*, 3247.
(202) Levin, Ya. A. *Dokl. Akad. Nauk SSSR* **1976**, *230*, 358.
(203) (a) Rykov, S. V.; Khudyakov, I. V.; Skakovsky, E. D.; Burrows, H. D.; Formosinho, S. J.; Miguel, M. G. M. *J. Chem. Soc., Perkin Trans. 2* **1991**, 835. (b) Rykov, S. V.; Khudyakov, I. V.; Skakovsky, E. D.; Tychinskaya, L. Yu.; Ogorodnikova, M. M. *J. Photochem. Photobiol.* **1992**, *A66*, 127. (c) Buchachenko, A. L.; Khudyakov, I. V.; Klimtchuk, E. S.; Margulis, L. A.; Yankelevitch, A. Z. *J. Photochem. Photobiol.* **1989**, *A46*, 281.
(204) Hommeltoft, S. I.; Berry, D. H.; Eisenberg, R. *J. Am. Chem. Soc.* **1986**, *108*, 5345.
(205) Garst, J. F.; Bockman, T. M.; Batlaw, R. *J. Am. Chem. Soc.* **1986**, *108*, 1689.
(206) (a) Taraban, M. B.; Leshina, T. V.; Salikhov, K. M.; Sagdeev, R. Z.; Moiin, Yu. N.; Margorskaya, O. I.; Vyazankin, N. S. *J. Organomet. Chem.* **1983**, *256*, 31. (b) Leshina, T. V.; D.Sc. Thesis, Institute of Catalysis, Siberian Branch of Russian Academy of Sciences, Novosibirsk, Russia, 1990.
(207) Step, E. N.; Tarasov, V. F. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 1738.
(208) Skakovsky, E. D.; Rykov, S. V.; Erdman, A. A.; Odelkop, Yu. A. *Dokl. Akad. Nauk BSSR* **1991**, *35*, 803.

(209) Podoplelov, A. V.; Stob, S.; Kaptein, R. *Chem. Phys. Lett.* **1989**, *160*, 233.
(210) Schilling, M. L. M. *J. Am. Chem. Soc.* **1981**, *103*, 3077.
(211) Jeevarajan, A. S.; Fessenden, R. W. *J. Phys. Chem.* **1992**, *96*, 1520.
(212) Evans, C. H.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 140.
(213) Buchachenko, A. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 2246.
(214) (a) Buchachenko, A. L.; Fedorov, A. V.; Yasina, L. L.; Galimov, E. M. *Chem. Phys. Lett.* **1984**, *103*, 405. (b) Step, E. N.; Tarasov, V. F.; Buchachenko, A. L.; Ustinov, V. I.; Grinenko, V. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, 200.
(215) Lehr, G. F.; Lawler, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 4048.
(216) Egorov, M. P.; Ezhova, M. B.; Kolesnikov, S. P.; Nefedov, O. M.; Taraban, M. B.; Kruppta, A. I.; Leshina, T. V. *Mendeleev Commun.* **1991**, 143.
(217) Buglas, J. C.; McLauchlan, K. *Isr. J. Chem.* **1989**, *29*, 39.
(218) Baxter, J. E.; Davidson, R. S.; Hageman, H. J.; McLauchlan, K. A.; Stevens, D. G. *J. Chem. Soc., Chem. Commun.* **1987**, 73.
(219) The MIE in sulfur was first claimed in: Step, E. N.; Tarasov, V. F.; Buchachenko, A. L. *Nature* **1990**, *346*, no. 6270, 25.
(220) Thomas, M. J.; Shackleton, T. A.; Wright, S. C.; Gillis, D. J.; Colpa, J. P.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1986**, 312.
(221) Wassink, B.; Thomas, M. J.; Wright, S. C.; Gillis, D. J.; Baird, M. C. *J. Am. Chem. Soc.* **1987**, *109*, 1995.
(222) Bockman, T. M.; Garst, J. F.; King, R. B.; Marko, L.; Ungvary, F. *J. Oranomet. Chem.* **1985**, *279*, 165.
(223) Seidler, P. F.; Bryndza, H. E.; Frommer, J. E.; Stuhl, L. S.; Bergman, R. G. *Organometallics* **1983**, *2*, 1701.
(224) (a) Nalesnik, T. E.; Orchin, M. *Organometallics* **1982**, *1*, 222. (b) Nalesnik, T. E.; Orchin, M. *J. Organomet. Chem.* **1981**, *222*, C5.
(225) Sakaguchi, Y.; Hayashi, H.; I'Haya, Y. J. *J. Phys. Chem.* **1990**, *94*, 291.
(226) Levstein, P. R.; van Willigen, H.; Ebersole, M.; Pijpers, F. W. *Mol. Cryst. Liq. Cryst.* **1991**, *194*, 123.
(227) Plüschau, M.; Zahl, A.; Dinse, K. P.; van Willigen, H. *J. Chem. Phys.* **1989**, *90*, 3153.
(228) Benn, R. *Chem. Phys.* **1976**, *15*, 369.
(229) Allen, R. B.; Lawler, R. G.; Ward, H. R. *J. Am. Chem. Soc.* **1973**, *95*, 1692.
(230) Sakaguchi, Y.; Hayashi, H.; I'Haya, Y. J. *J. Photochem. Photobiol.* **1992**, *A65*, 183.
(231) Lawler, R. G.; Livant, P. *J. Am. Chem. Soc.* **1976**, *98*, 3710.
(232) Benn, R.; Wilke, G. *J. Organomet. Chem.* **1979**, *174*, C38.
(233) Turro, N. J.; Khudyakov, I. V.; Gopidas, K. R. *Chem. Phys.* **1992**, *162*, 131.
(234) Kramer, A. V.; Osborn, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 7832.
(235) Kaptein, R.; Van Leeuwen, P. W. N. M.; Huis, R. *J. Chem. Soc., Chem. Commun.* **1975**, 568.
(236) Khudyakov, I. V.; Turro, N. J. *Res. Chem. Intermed.* **1993**, *19*, no. 1.
(237) Nikitenko, S. I.; Gai, A. P.; Glazunov, M. P.; Krot, N. N. *Dokl. Akad. Nauk SSSR* **1990**, *312*, 402.
(238) Sakaguchi, Y.; Hayashi, H. *J. Phys. Chem.* **1986**, *90*, 550.
(239) Hayashi, H.; Sakaguchi, Y.; Murai, H.; I'Haya, Y. J. *J. Phys. Chem.* **1986**, *90*, 4403.
(240) Sakaguchi, Y.; Hayashi, H.; Murai, H.; I'Haya, Y. J.; Mochida, K. *Chem. Phys. Lett.* **1985**, *120*, 401.
(241) Sakaguchi, Y. Private communication, 1992.
(242) Podoplelov, A. V.; Sen Chel Su; Sagdeev, R. Z.; Stein, M. S.; Moralev, V. M.; Goldanski, V. I.; Molin, Yu. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, 2207.
(243) van Willigen, H.; Vuolle, M.; Dinse, K. P. *J. Phys. Chem.* **1989**, *93*, 2441.
(244) Prisner, T.; Dobbert, O.; Dinse, K. P.; van Willigen, H. *J. Am. Chem. Soc.* **1988**, *110*, 1622.
(245) Bowman, M. K.; Toporowicz, M.; Norris, J. R.; Michalski, T. J.; Angerhofer, A.; Levanon, H. *Isr. J. Chem.* **1988**, *28*, 215.
(246) Yamauchi, S.; Ueda, T.; Satoh, M.; Akiyama, K.; Tero-Kubota, S.; Ikegami, Y.; Iwaizumi, M. *J. Photochem. Photobiol.* **1992**, *A65*, 177.
(247) (a) Lendzian, F.; von Malzan, B. *Chem. Phys. Lett.* **1991**, *180*, 191. (b) Lendzian, F.; Schlüpmann, J.; von Gersdorff, J.; Möbius, K.; Kurreck, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1461.
(248) Podoplelov, A. V.; Leshina, T. V.; Sagdeev, R. Z.; Molin, Yu. N.; Goldanski, V. I. *Pis'ma. Zh. Eksp. Teor. Fiz.* **1979**, *29*, 419.
(249) (a) Goldwasser, M.; Dutel, J. F.; Naccache, C. *Zeolites* **1989**, *9*, 54. (b) Gustafson, B. L.; Lin, M.; Lunsford, J. H. *J. Phys. Chem.* **1980**, *84*, 3211. (c) Reynolds, P. A.; Delfs, C. D.; Figgis, B. N.; Engelhardt, L. M.; Moubaraki, B.; Murray, K. S. *J. Chem. Soc., Dalton Trans.* **1992**, 2029.
(250) Steiner, U. E. Private communication, 1992.
(251) In fact $Ru(bpy)_3^{3+}$ oxidized SL with the formation n-$C_{11}H_{23}CO_2^{\bullet}$; the latter radical should rapidly convert into a corresponding alkyl radical. (Khudyakov, I. V. Unpublished results, 1992). Quite probably this alkyl radical remains in the micelle. However, MV^+ escapes the SL micelle (ref 233), and it is difficult to suggest any micellized RP in this system, which can manifest MFE. If MFE originates in random pairs in nonviscous aqueous solutions, it should be much less than that observed in ref 233. (See: Margulis, L. A.; Khudyakov, I. V.; Kuzmin, V. A. *Chem. Phys. Lett.* **1986**, *124*, 483.) Further experiments should allow a deeper understanding of this photoinduced electron transfer in micellar solutions.
(252) Breslin, D. T.; Saeva, F. D. *J. Org. Chem.* **1988**, *53*, 713.
(253) The observed effect is related to the SOC quenching and not to the appearance of a Coulomb repulsion of radical anions $\mathcal{A}^{\bullet-}$ and $X_2^{\bullet-}$. Among the classes of systems under investigation there were also pairs $[\mathcal{A}^{\bullet},X^{\bullet}]$ and $[\mathcal{A}^{\bullet-},X_2^{\bullet-}]$, and the same regularities have been observed for these pairs (refs 38 and 47).
(254) (a) Connolly, J. M. *Organometallics* **1984**, *3*, 1333. (b) Grissom, C. B. In *Magnetic and Spin Effects in Chemistry and Related Phenomena. Book of Abstracts*; University of Konstanz: Konstanz, Germany, 1992; p 13.
(255) Lei, X.; Zhao, G.; Liu, Y.; Turro, N. J. *Langmuir* **1992**, *8*, 475.
(256) Koptyug, I. V.; Lukzen, N. N.; Bagrayanskaya, E. G.; Doktorov, A. B.; Sagdeev, R. Z. *Chem. Phys.* **1992**, *162*, 165.
(257) Sagdeev, R. Z.; Bagryanskaya, E. G. *Pure Appl. Chem.* **1990**, *62*, 1547.
(258) Tague, T. J.; Wight, C. A. *J. Am. Chem. Soc.* **1992**, *114*, 9235.
(259) Steiner, U. E.; Baumann, D.; Haas, W. In *Dynamics and Mechanisms of Photoinduced Transfer and Related Phenomena*; Mataga, N., Okada, T., Masuhara, H., Eds.; Elsevier: Amsterdam, 1992; p 275.