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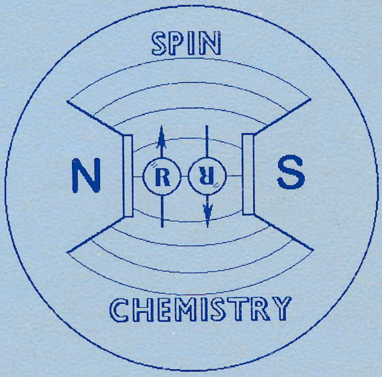
International Tomography Center
Siberian Branch, Russian Academy of Sciences

IV International Symposium on Magnetic Field and Spin Effects in Chemistry and Related Phenomena



Novosibirsk, Russia
August 18-23, 1996

Abstracts and Program.

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PREFACE

Welcome! The Organizing Committee of *IV International Symposium on Magnetic Field and Spin Effects in Chemistry and Related Phenomena* is pleased to welcome you in Novosibirsk. We are honored to have with us such a highly competent audience and we are impressed for the long distances most of you went to attend this meeting.

This volume contains the abstracts of the invited lectures, short talks, and posters which will be presented at the Symposium. The abstracts have been reproduced without editing from the camera-ready copy provided by authors. The breadth and quality of the science briefly summarized in the abstracts contained in this volume provides ample evidence for the current vigor of research in spin chemistry.

We acknowledge with gratitude the generous financial support of sponsors whose names appear in the previous page. In particular we are indebt to the Russian Foundation for Basic Research and Bruker Analitische Messtechnic GmbH for their most generous contributions.

The social program of the Symposium includes excursions to Scientific Institutes of Akademgorodok, sightseeing excursion to Novosibirsk city, boat excursion on Ob-river, concert of chamber music, and tours to St.-Petersburg and Baikal lake. Thus, during the Symposium you can get acquaintance with both Russian science and culture. We hope the participants will enjoy their stay in our city and the scientific discussion which we will have during the Symposium.

The Organizing Committee

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International Tomography Center
Social program

INVITED

TALKS

Spin catalysis: experiment

Anatoly L.Buchachenko[a], Vitaly L.Berdinsky[b]
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Spin catalysis as a new spin phenomenon manifests itself in the radical pair recombination, ortho-para positronium conversion, cis-trans isomerization of molecules with double bonds, the recombination of spin polarized hydrogen atoms at cryogenic temperatures, etc. In contrast to the well known magnetic effects in spin chemistry spin catalysis is induced by nonmagnetic, exchange interaction.

The direct experimental evidences of spin catalysis has been obtained in the photolysis of 2,4-diphenylpentan-3-one in the presence of nitroxide radicals, which were shown to enhance the recombination probability of the radical pairs generated by photolysis[1]. Similarly the recombination probabilities of the nitroxide biradicals with alkyl radicals exceed those for nitroxide monoradicals[2]. The rate constants of the radical pair spin transformation catalyzed by organic radicals exceed those of noncatalytic spin transformation at least by an order of magnitude[3]. The catalytic efficiency of paramagnetic lantanide ions is much lower than that of organic radicals and is linearly dependent on the electron spin of ions[4-6].

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SPIN POLARIZATION IN FULLERENE DERIVATIVES IN DOUBLET, TRIPLET AND QUARTET STATES

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In the recent years a number of examples of spin polarization effects have been reported, deriving from the interaction of excited triplet state molecules with free radicals [1-3]. The effect occurs via the formation of triplet-radical pairs and the mixing of the pair doublet and quartet wave functions [4]. The triplet-radical pair mechanism (TRPM) of electron spin polarization takes place in liquid solutions during the encounter of the diffusing radical and excited state molecules. It can be also active in crystalline solids if diffusing excitations (triplet excitons) interact with trapped free radicals [5,6]. In both cases the formation of the pair is observed by its effect on the anomalous intensity of the radical EPR lines, which occur either in enhanced absorption or in emission. The interacting pair is too short-lived for allowing for its observation.

An idea for increasing the pair lifetime is to join together triplet and radical in the same molecular unit by a chemical bond. We have considered a molecule containing a stable nitroxide free radical connected to a fullerene C_{60} derivative, the latter acting as triplet precursor. Triplet-radical pair is then formed without the need of diffusion processes whenever a light quantum is absorbed and there is crossing to the triplet state [7].

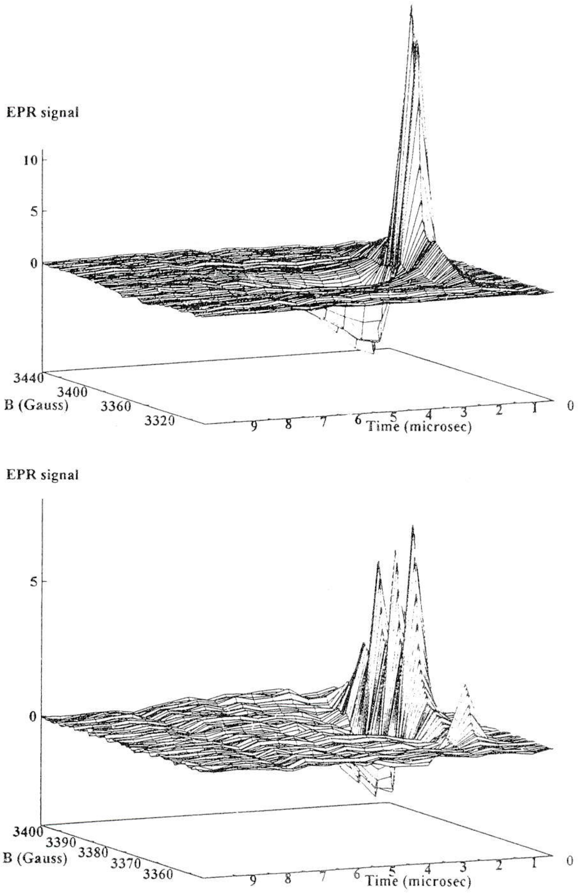
In this communication we present the results for a series of nitroxide substituted C_{60}.In these systems we have observed spin polarization of the radicals in the doublet electronic ground state, caused by the TRPM. We observed also transient EPR signals due to the spin polarized excited quartet states of the interacting pair.

C_{60} is known to give rise to excited triplet states with a high yeald by absorption of a visible or UV light quantum. This characteristic has been shown also in substituted C_{60} like fulleropyrrolidines [8]. Moreover ISC in fullerene C_{60} and derivatives is spin selective, giving rise to strongly spin polarized triplet spectra. This fact offers the opportunity to investigate the effect on TRPM of spin polarization of the pair triplet partner.

Time resolved EPR measurements of spin polarization in fulleropyrrolidines in its first excited triplet state produced by a LASER pulse will be discussed together with the analysis of the transient polarization of the nitroxide substituted compounds.

Figure 1 a shows an example of the complete time-magnetic field two-dimensional frozen solution EPR signal of a fulleropyrrolidine nitroxide in the quartet excited state. In the liquid solution spectrum reported in Figure 1b the quartet state spectrum is superimposed to the signal arising from the spin polarized nitroxide in the electronic ground doublet state.

Figure 1



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Spin Dependent Electronic Processes in Semiconducting Polymers: Study by MFE and RYDMR techniques

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The talk will be devoted to possibilities of application of the magnetic field spin effect (MFE) for studying electronic processes in organic photoconducting solids and new examples of spin dependent processes in photoconductivity and luminescence of poly(vinylene phenylene) (PPV).

1. Introduction

The next topics will be considered [1-3]:
Photoconductivity of organic semiconductors: general schemes and magnetic field sensitive processes. # Estimation of the mobility of charge carriers. # Determination of the delocalisation length for charge carriers in π-conjugated polymers (poly(diacetylene)), poly(arylene vinylene)). The approach is based on the temperature dependence of the MFE on the photoconductivity: energy barrier is measured for the process of the separation of a pair of charge carriers from the state with exchange interaction (CT exciton). # Diffusion length of charge carriers may be measured before they become trapped or recombine. The technique is based on the electric field dependence of the MFE.
Position of the energy level which corresponds to electronic excited state responsible for the electroluminescence of polymers. Technique is based on studying the temperature dependence of the MFE on the intensity of . fluorescence of the material.
Mechanism of an oxygen effect on the photoconductivity of organic polymers may be studied. The possibility is connected with the spin-dependent reaction of triplet excitons with oxygen molecules.

2. Photoconductivity of PPV in the Air. MFE and Mechanism of Generation and Recombination of Charge Carriers.

Two types of MFE on the photocurrent were revealed in samples of PPV: Prompt one is connected with existence of polaron pairs as precursors for photoconductivity. The second MFE is delayed one and is shown to be connected with the reaction of triplet and singlet excitons with O_2 [4]. The reaction changes inertially the concentration of O_2 molecules in the bulk of the polymer, its rate being dependent on magnetic field. Positive mobile charge carriers responsible for the photocurrent are produced in the reaction of dissociation of primary singlet excitons by oxygen, photooxidation products and other weak dopants like C_{60} molecules. The probability of charge carrier generation in the reaction with O_2 molecule is found to be higher than with C_{60} clusters. An enhancement of the photoconductivity of PPV in the air is connected with that factor and also with significant increase of the life time of charge carrier before recombination. Recombination of positive charge carriers with oxygen negative ions is very slow giving a quasi persistent photoconductivity of the polymer in the air.

3. Polaron Pairs and Their Transformations in PPV.

Photoluminescence of films of poly (*p*-phenylene vinylene), and changes of its intensity under conditions of electron spin resonance as a function of temperature, light intensity, microwave power, *etc.* were studied [5].

The technique based on the modulation of the spin state of pairs of paramagnetic species by resonant transitions between Zeeman sublevels of the pairs that have a dynamic spin polarisation. This is a technique that was introduced originally as Reaction Yield Detected Magnetic Resonance. Three types of resonant signals have been revealed in the magnetic resonance spectrum namely a narrow (13 G half width), and a broad (1200 G) ones at $g = 2$, and a signal at $g = 4$. The results obtained have permitted to conclude that Coulomb bound polaron pairs are produced with a high yield under the 488 nm photoexcitation of PPV. The narrow signal was shown to appear due to a microwave induced resonant transitions in triplet polaron pairs. The resonant transitions changed the rate of geminate recombination of the pairs which was revealed to lead to formation of triplet intra-chain excitons. Those excitons annihilate in the second order reactions showing themselves as delayed fluorescence. Annihilation rate was seen to be influenced by resonant transitions in triplet exciton pairs as well. Life time of triplet intra-chain excitons was estimated from modulation frequency dependence. Results show that energy level of lowest polaron pair state situated below that of singlet intra-chain exciton can act as a sink of the excitation energy influencing the quantum yields of the photoluminescence, electroluminescence and photoconductivity.

Acknowledgements

The author is indebted to all his colleagues, mentioned in the References, on results of collaboration with whom the present talk is based.

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5. Evidences for triplet inter-chain polaron pair in PPV and their transformations. V. Dyakonov, G. Roessler, M. Schwoerer, and E.L. Frankevich. *Phys. Rev.* **B** (submitted, 1996)

SPIN PROCESSES IN PHOTOSYNTHETIC REACTION CENTERS CONTAINING Ni-BACTERIOCHLOROPHYL

Maria E.Michel-Beyerle

Technische Universität München

TIME-RESOLVED TRANSIENT-ABSORPTION-DETECTED MAGNETIC RESONANCE SPECTRUM OF INTERMEDIATE BIRADICAL IN THE POLYMETHYLENE LINKED HYDROGEN DONOR ACCEPTOR SYSTEM.

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1. Introduction

We applied the transient-absorption-detected magnetic resonance spectroscopy to the polymethylene-linked xanthone (hydrogen acceptor) and xanthene (hydrogen donor) (XO-(n)-XH_2, where n=12). In this linked system, biradical generated by the intramolecular hydrogen abstraction reaction does not escape to free radicals, and therefore, we can analyze the spin dynamics of the radical pair without the perturbation of free radical..

2. Experimental

Sample placed inside of the ESR cavity was excited by 266 line of a YAG laser. The transient absorption spectrum of the biradical generated by the intramolecular hydrogen transfer was monitored at 355 nm (which is mainly the peak of the xanthyl radical). The microwave pulse generated by a gun diode and a PIN switch and amplified by a TWTA was introduced to the cavity. By microwave, the absorptivity either increases or decreases. The transient absorption-detected magnetic resonance spectrum was obtained by plotting the difference of the absorptivity as a function of the external magnetic field.

3. Results and Discussion

The time dependence of the transient-absorption-detected ESR spectrum is shown in Figure 1. Since the intermediate biradical is generated from the triplet excited state of the xanthone part, (i.e. ,triplet precursor) the positive sign of the spectrum represents the spin locking effect and the negative sign represents the acceleration of the intersystem crossing due to the pumping of the population between the triplet sublevels. The observed spectrum shows that the spin locking effect is effective at around 347 mT and the acceleration of the intersystem crossing is effective in very side range of the magnetic field (300～380 mT). Immediately after the laser excitation, only the spin locking effect is observed. In contrast, the effect of the acceleration is observed after 100 ns, and it exists for a long time.

The time profile of the signal at 347.1 mT is shown in Figure 2. Since the scavenging and the escape of the radical pair is negligible, the time derivative of the concentration of the intermediate biradical (tr ρ), which is proportional to the intensity of the transient absorption, is represented as follows:

$$\frac{\partial\left(A_{on}-A_{off}\right)}{\partial t} \propto \frac{\partial\left(\mathrm{tr}\,\rho_{on}-\mathrm{tr}\,\rho_{off}\right)}{\partial t} = -K_S\left\{\left\langle S\right|\rho_{on}(t)\left|S\right\rangle-\left\langle S\right|\rho_{off}(t)\left|S\right\rangle\right\}$$

Namely, the slope of the time profile should represent the effect of the microwave on the probability of finding the singlet spin state. Therefore, the positive slope observed before 200 ns shows that the spin locking effect is dominant at earlier time. As is understood in Figure 2, the spin locking effect disappears after 200 ns even though the system is under the strong microwave irradiation.

In order to understand the spectral behavior, we have made the model calculation based on the two site model. From the comparison with the experimental data, we conclude that the signal observed beyond the center are due to the "forbidden" transitions from T+ or T- state to the S state and that the spectral shape reflects the fluctuation of the exchange interaction.

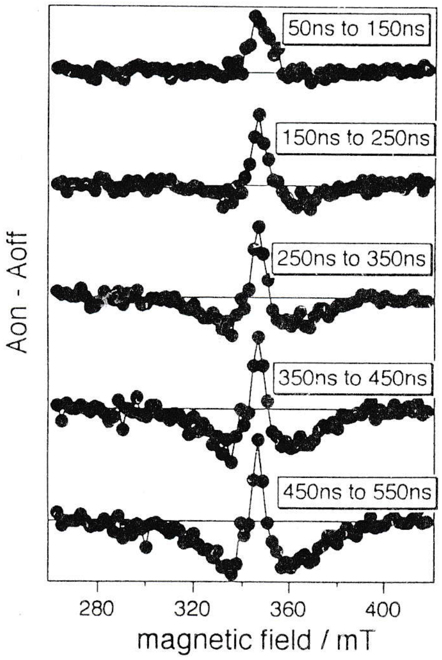

Figure 1

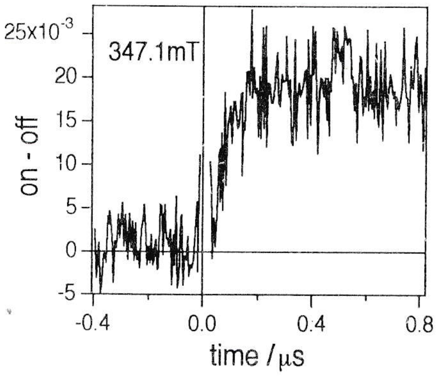

Figure 2

CIDEP after Laser Flash Photolysis of Azoalkanes in Solution

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After direct photoexcitation, dialkylazo compounds undergo trans-cis isomerization and/or cleavage into two alkyl radicals and N_2. The reactions occur from an excited singlet state. Consequently, the time-resolved EPR spectra of the alkyl radicals exhibit an initial emission/absorption (A/E) type antiphase spin polarization which, at longer times, is replaced by the usual E/A multiplet polarization, generated in the F-pairs. Isomerization and/or scission also occur, if the azo compounds are triplet sensitized. Then, the initial spin polarization is an E/A geminate pair multiplet effect, superposed by the spin polarization in the triplet precursor molecule. The magnitudes of these polarizations have been determined quantitatively for some systems, and two aspects will be discussed:

1. The ratio of the initial geminate pair to the F-pair polarization after direct azo photolysis turns out to be a very sensitive probe for the initial separation of the two species in the geminate pair. A plausible theoretical model for the initial distance distribution after these exothermic cleavage reactions ($\Delta H \approx 240$ kJ/mol) is found, which predicts correctly the polarizations as well as the in-cage recombination ("cage-effect") in dependence on viscosity.

2. The triplet sensitized cleavage of dialkylazo compounds is utilized to probe the spin polarization in some ketone triplet molecules. The experimental results indicate the presence of an unusual polarization mechanism.

Stimulated and Optical Nuclear Polarization Studies with Nanosecond Time Resolution

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The generation of non-Boltzmann nuclear spin order as a result of photoexcitation has for many years been utilized to gain detailed information on the individual steps of photoprocesses in solid and liquid reaction systems. Due to the comparatively long nuclear spin-lattice relaxation times in diamagnetic photoproducts this spin order is efficiently accumulated and allows sensitive detection. Hence, it is an observable particularly suited for the investigation of short-lived intermediates which are involved in the polarization process. Irradiation of rf-fields near spin resonance of paramagnetic intermediates allows spectroscopy of such species. While in solid systems the term rf-ONP or MI-ONP (rf- and Microwave Induced Optical Nuclear Polarization resp.) is used for this technique, SNP (Stimulated Nuclear Polarization) is more common for the study of liquid systems.

When applying rf-pulse sequences in synchronization with the light excitation the time evolution of the photoprocess can be mapped out. As the encoding of time information is completely separated from the observation, one avoids receiver deadtime and can achieve time resolution of a few nanoseconds. In this regime the spin dynamics is dominated by coherent motion, which is reflected in transient oscillations in the photoprocess.

For the case of a crystalline system we were able to determine *the full set of oscillatory contributions and relate them to the corresponding coherent modes.* As a result, a purely quantum-dynamical description of the polarization transfer process could be established without any of the usual thermodynamical approximations. It is used to give a comprehensive interpretation of various results, which have been controversely discussed in the literature.

In liquid state reaction systems we used ^{1}H and ^{13}C SNP to study geminate processes, in particular the interaction of spin and molecular dynamics in biradical reactions. The rise and decay characteristics of SNP and its dependence on environmental conditions such as viscosity and temperature as well as on molecular parameters and external fields has been investigated and been used to develop a detailed picture of the photoreaction.

SPIN POLARIZATION AT LARGE VALUE OF MAGNETIC RESONANCE PARAMETERS

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The current state of the art in the studies of chemically induced dynamic electron (or nuclear) polarization (CIDEP (or CIDNP)) of geminate radical pairs (RP) calls for adequate theoretical calculations covering a wide variation range of magnetic resonance parameters (spin-Hamiltonian parameters). The most simple way of calculating these effects is based on numerical solution of the stochastic Liouville equation (SLE). However, in considering complicated systems, considerable difficulties arise both in obtaining and in physical interpretation of numerical solutions.

That is why, recently, a number of analytical computational methods have been developed. When applied to simple systems, they give rather accurate and physically interpretable results, and, if combined with numerical calculations, allow one to consider fairly complicated systems.

The recently developed method [1] based on the idea to split the spin-Hamiltonian into two parts and the Green function method [2] are the most advanced analytical techniques. In the present paper we analyze, with the CIDEP calculation in the two-state STo approximation as an example, the potentialities and accuracy of these two methods by comparing them with numerical calculations made by very accurate and efficient method developed in [3].

The method of spin-Hamiltonian splitting has been developed in [1] with the restriction of not very strong STo-mixing. Strong STo-mixing has been considered in [4] in the framework of the exchange interaction perturbation theory. This corresponds to rather small values of the exchange integral. This is just the case where the agreement with numerical calculations takes place. However, as the exchange integral increases, apparent disagreement with numerical calculation results is observed even at not very strong STo-mixing.

At the same time, it has been shown that the Green functions method using just the exchange integral decay sharpness makes it possible to obtain highly accurate solutions valid over a wide variation range of spin-Hamiltonian parameters, including large values of these parameters. It is essential that the method allows one to easily include into consideration contact reaction of RP radicals proceeding at arbitrary prescribed rate, as well as the process of contact dephasing of their spin states. The method also admits generalization aimed at taking account of complicated RP structure and the character of internal motion of radicals.

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CIDNP, CIDEP AND FLASH-PHOTOLYSIS STUDIES OF PHOTOREACTIONS INVOLVING ^{31}P-CENTERED RADICALS

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The photochemistry of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TMBDPO), bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide (BAPO) and p-acetylbenzyl dimethyl phosphite (ABDPI) and related compounds has been studied by means of CIDEP, CIDNP, time-resolved (TR) UV and IR spectroscopies and product analysis. The importance of the photochemistry of TMBDPO and BAPO stems from their use as polymerization photoinitiators. ABDPI shows unusual photochemistry in that unlike other benzyl phosphites which undergo photo-Arbuzov rearrangement via a singlet radical pair (RP) or concertedly, ABDPI reacts from its triplet state to a significant extent. All three compounds yield phosphorus-centered free radicals upon direct photoexcitation with UV light.

TMBDPO is known to undergo α-cleavage from the triplet state to yield diphenylphosphonyl and trimethylbenzoyl radicals. The addition of diphenylphosphonyl radical to various unsaturated compounds has been reported in detail. However, there is little information available on the reactions of diphenylphosphonyl radical with hydrogen and halogen atom donors, the reactivity of trimethylbenzoyl radical, as well as on the products formed in the presence and in the absence of radical trapping agents. This work reports direct time-resolved study of trimethylbenzoyl radical by TR IR and of phoshponyl radical by TR UV spectroscopies. Analysis of the pseudo-first order kinetics allowed us to determine the rate constants for the reactions of these radicals with $BrCCl_3$, PhSH, and Ph_2CHOH. Product studies have revealed the main reaction products and confirmed that the radicals react with $BrCCl_3$ and PhSH via atom abstraction.

BAPO belongs to a new class of polymerization photoinitiators, bis(acyl)phosphine oxides, introduced recently. Their advantage is a red-shifted UV absorption spectrum and an ability to generate four radicals per initiator molecule. The primary reaction is shown to be an α-cleavage form a triplet state which yields 2,6-dimethoxybenzoyl-2,4,4-trimethylpentylphosphonyl and 2,6-dimethoxybenzoyl radicals. Transient absorption in the range 425-500 nm detected in this work is assigned to the former radical. The rate constants for the reactions of this phosphonyl radical with a number of halocarbons, alkenes and oxygen are measured and compared with those for the diphenylphosphonyl radical formed upon photolysis of TMBDPO. The rates for 2,6-dimethoxybenzoyl-2,4,4-trimethylpentylphosphonyl radical are usually 2-6 times lower than those for diphenylphosphonyl radical towards the same compounds. This is attributed to a more planar structure with less s-character of the former radical, which is confirmed by our TR ESR data. The rate constants for reaction of both phosphonyl radicals with acrylates show substantial steric effect. Halogen atom abstraction rates correlate inversely with the strength of the carbon-halogen bond.

The formation of both 2,6-dimethoxybenzoyl-2,4,4-trimethylpentylphosphonyl and 2,6-dimethoxybenzoyl radicals upon BAPO photolysis is confirmed by our TR ESR studies. At short delays the former radical exhibits an E/A* CIDEP pattern, similar to TMBDPO photolysis, which indicates that the radicals are derived from the triplet state of

BAPO. The hfcc on phosphorus, A(P)=285 G, is smaller than that for diphenylphosphonyl radical (370 G), implying less s-character for the former radical.

The addition of both phosphonyl radicals to alkenes can be readily detected by TR ESR. Their reactions with styrene yield polarized ESR spectra of corresponding adducts. Spectral analysis and identification of radicals are greatly facilitated on going from styrene to 2,4,6-trimethoxystyrene. In the case of BAPO photolysis TR ESR spectra demonstrate the ability of this type of photoinitiators to yield *four* radicals upon irradiation.

Benzylic dimethyl phosphites, such as benzyl dimethyl phosphite (BDMPI), 1-naphthylmethyl dimethyl phosphite (NMDPI), etc., undergo rearrangement to respective phosphonates concertedly or via a short-lived singlet RP upon direct photolysis. However, direct photolysis of ABDPI and triplet-sensitized reaction of NMDPI produce significant amounts of products of free radical reactions and only small amounts of phosphonates, which suggests that in both cases the reaction proceeds via a triplet RP. Photolysis of ABDPI in benzene gives additional products derived from the reaction of the dimethoxyphosphonyl radical with the solvent. Addition of PhSH significantly suppresses formation of radical escape products in favor of products of reaction with PhSH.

The triplet reaction channel for ABDPI was verified in our TR CW and FT ESR experiments. Neither BDMPI nor NMDPI show any detectable ESR signals upon direct photolysis. On the contrary, contributions of both dimethoxyphosphonyl and *p*-acetylbenzyl radicals can be readily identified in the well-resolved TR ESR spectra obtained upon photolysis of ABDPI. CIDEP patterns for both radicals are in agreement with the *triplet* multiplicity of the primary RP, exhibiting net emissive contribution due to triplet mechanism and/or T_--S mechanism of CIDEP formation superimposed upon E/A polarization due to T_0-S mechanism. Kinetic studies in combination with dynamic polarization recovery experiment demonstrate an efficient polarization generation in the free encounters of radicals that escape from primary RP. The significant involvement of the triplet channel is further verified by the observation of dimethoxyphosphonyl radical with similar polarization pattern upon triplet-sensitized photolysis of NMDPI.

CIDEP results obtained upon direct photolysis of ABDPI and sensitized photolysis of NMDPI implicate the involvement of T_--S mechanism of ISC in the evolution of RPs containing P-centered radicals which possess large hfcc (for dimethoxyphosphonyl radical A(P)=700 G). This finding is further evidenced by the observation of steady-state ^{31}P CIDNP upon ABDPI photolysis in the presence of effective scavengers (CCl_3Br, $PhCH_2Br$, PhSH, etc.) of *p*-acetylbenzyl radicals escaping from primary RP. While the main incage product, phosphonate, is always absorptively polarized, the polarization of products formed upon trapping of escaped dimethoxyphosphonyl radicals is absorptive at 58.8 kG, but becomes emissive at 18.8 kG. This is attributed to the switching of the predominant ISC mechanism from T_0-S in higher fields to T_--S in lower magnetic fields.

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MAGNETIC FIELD DEPENDENCE OF VITAMIN B_{12} DEPENDENT PHOTOCHEMICAL AND ENZYMATIC REACTIONS

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The RP produced by homolysis of the C-Co bond in vitamin B_{12} and its analogues undergoes magnetic field dependent recombination in chemical and biological systems.

Chemical Systems. Photodissociation of adenosylcob(III)alamin or methylcob(III)alamin produces the alkyl radical and cob(II)alamin as a singlet RP. The continuous-wave photochemical quantum yield decreases by a factor of two in viscous solvents in the range 0.05 - 1 T due to a decrease in intersystem crossing rate induced by hyperfine coupling from Co(II) ($A(^{59}Co) \cong 8$ mT; $I = 7/2$) (1-4). For adenosyl-cob(III)alamin, recombination in the geminate RP can be observed directly by picosecond laser flash photolysis. The first-order rate of geminate RP recombination is independent of viscosity, but increases from 1×10^9 s^{-1} at B=0 T, to 4×10^9 s^{-1} at B=0.05 T. The observed magnetic field dependence is consistent with the RP being formed in the singlet spin state with a magnetic field dependent increase in recombination arising from a decrease in intersystem crossing rate in the RP that partially populates the triplet state at the expense of the singlet population. In spite of the four-fold increase in RP recombination in the geminate RP at 0.05 T, the magnetic field dependence of the continuous-wave photochemical quantum yield is due to changes in recombination in the diffusive RP (5). The diffusion model of RP with semiclassical approximation of spin dynamics in RP has been applied successfully to simulate the observed magnetic field dependence (6). Photo-CIDNP studies of alkylcobalamin analogues assign the spin multiplicity of the precursor RP as singlet (7).

Enzymatic Systems. Adenosylcob(III)alamin is a cofactor for approximately 12 enzymatic reactions in humans and bacteria. The steady-state and transient kinetics of one B_{12} dependent enzyme, ethanolamine ammonia lyase, exhibit a profound magnetic field dependence in the range 0-0.4 T in a manner that is consistent with 5'-deoxyadenosyl radical : cob(II)alamin RP recombination being the magnetic field dependent process. The steady-state kinetic parameter, V_{max}/K_m, decreases by 25% at 0.1 T with unlabeled ethanolamine (substrate), and V_{max}/K_m decreases by 60% at 0.12 T with deuterated ethanolamine (8). The larger magnetic field effect with deuterated substrate reflects a greater recombination of the 5'-deoxyadenosyl radical : cob(II)alamin RP. The tritium isotope effect, ${}^{T}(V_{max}/K_m)$, exhibits an even larger magnetic field dependence, with the maximum effect observed at 0.2 T (9). The net rate of cob(II)alamin formation in the enzyme active site (along with implicit RP recombination) can be observed by stopped-flow spectrophotometry (10). In the enzyme active site, the net rate of cob(II)alamin formation decreases by 25% in the range 0.05 T.

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SPIN CHEMISTRY OF PARAMAGNETIC INTERMEDIATES FORMED IN THE PHOTOLYSIS OF 7-SILA(GERMA)NORBORNADIENES

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Chemistry of organometallic compounds with IV Group elements (Si, Ge, Sn, Pb) is intensively developing field of research. Particular interest to these species is defined by their practical importance in microelectronics (Si, Ge), national economy (Si), and medicine (Ge, Sn) [1].

Heavy carbene analogs (silylenes, germylenes, and stannylenes) are reactive paramagnetic species playing an important role in a number of organic syntheses [2]. Research into the mechanisms of formation and decay of carbene analogs with IV Group elements is one of the basic problems of modern organometallic chemistry [2]. Spin chemistry methods have already contributed significantly to the studies on structure and reactivity of paramagnetic intermediates formed in a number of organometallic reactions [3,4]. At present, these techniques appear to be the sole direct methods of detection, e.g., of the multiplicities of reactive states.

The present report is devoted to the investigations of paramagnetic species formed in the photolysis of 7,7′-dimethyl-7-sila(germa)norbornadienes (I and II, respectively) by means of spin chemistry methods (^{1}H CIDNP and magnetic field effects). These compounds are used in organometallic chemistry as basic precursors of dimethylsilylenes and dimethylgermylenes.

Analysis of ^{1}H CIDNP effects observed for initial I and II and their photo-decomposition products has allowed to propose the scheme of radical stages of the process. In the frames of this scheme, biradical species have been suggested to be the precursors of main reaction products, tetraphenylnaphthalene and dimethylsilylene (-germylene). Biradicals result from carbon-element bond breaking in singlet excited state of I and/or II.

Involvement of paramagnetic precursors in the reaction is also confirmed by magnetic field influence on tetraphenylnaphthalene yield observed in the photolysis of 7-silanorbornadiene (I). Analysis of field dependence of magnetic effect observed in laser pulse photolysis experiments has allowed to assume that this paramagnetic precursor is above mentioned biradical.

^1H CIDNP has also made it possible to detect the reactions of triplet dimethylsilylene and dimethylgermylene with various radical scavengers. Note that to date the existence of heavy carbene analogs with IV Group elements has been only postulated in the literature on the basis of quantum chemical calculations [2].

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CROSS-RELAXATION MECHANISM OF CIDNP FORMATION IN REACTIONS OF 2-HYDROXY-2-PROPYL RADICALS

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The cross-relaxation mechanism of CIDNP formation involves the transfer of the electron polarization, formed by triplet (TM) or radical pair (RPM) mechanisms, to the nuclear subsystem due to electron-nuclear cross-relaxation. On radical recombination, the nuclear polarization manifests itself as the absorptive or emissive NMR signals of diamagnetic reaction products. In this work, we studied the influence of scalar cross-relaxation on a formation of net nuclear polarization in reactions involving 2-hydroxy-2-propyl radicals by time-resolved CIDNP method.

2-Hydroxy-2-propyl radicals have been generated by different methods: the photolysis of 2,4-dihydroxy-2,4-dimethylpentan-3-one (1), the photolysis of acetone in isopropanol (2), and the photolysis of di-*tert*-butylperoxide in isopropanol (3):

$$\mathrm{HO(CH_3)_2-CO-C(CH_3)_2OH \xrightarrow{h\nu} HO(CH_3)_2-\dot{C}O + (CH_3)_2\dot{C}OH} \quad (1)$$

$$\mathrm{(CH_3)_2CO + (CH_3)_2CHOH \xrightarrow{h\nu} 2(CH_3)_2\dot{C}OH} \quad (2)$$

$$\mathrm{(CH_3)_3C-O-O-C(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3C-\dot{O}} \quad (3)$$

$$\mathrm{(CH_3)_3C-\dot{O} + (CH_3)_2CHOH \longrightarrow (CH_3)_3COH + (CH_3)_2\dot{C}OH} \quad (3a)$$

In reaction (1), geminate radical pairs with $\Delta g \neq 0$ are formed. Spin evolution of these pairs leads to formation of both net CIDNP and net CIDEP by RPM. In bulk processes, electron polarization is transferred to the nuclear one, and nuclear polarization of the bulk products differs significantly from the geminate polarization.

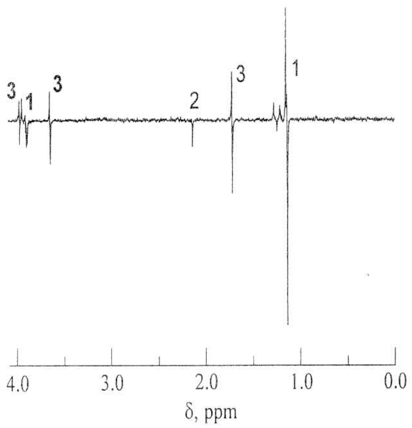

Fig.1. CIDNP spectrum obtained during the photolysis of acetone in isopropanol: 1-isopropanol, 2-acetone, 3-enol

In reactions (2) and (3), only 2-hydroxy-2-propyl radicals are present in solution (reaction (3a) is fast), and neither net CIDNP nor net CIDEP can be formed due to RPM. However, in CIDNP spectra the net emission is observed for all the reaction products: isopropanol, acetone, enol, and pinacol. Analysis of CIDNP kinetics in microsecond time scale allows us to conclude that the main source of

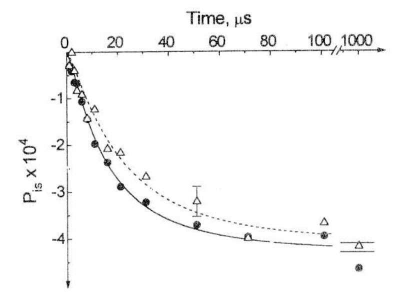

Fig. 2. Kinetics of the net polarization of the CH_3 protons of isopropanol: ● - experimental points, solid line - calculation for the initial concentration of radical pairs 4.4x10^{-5} M; Δ - experimental points, dashed line - calculation for the initial concentration 2.2x10^{-5} M.

nonequilibrium electron polarization is chemical reaction itself. The mechanism of the formation of the electron polarization is based on the selection rule for radical recombination (or disproportionation): only the radicals with untiparallel spin orientation (the singlet spin state) can recombine. Thus, the total net electron polarization (i.e., the difference in the populations of the levels with S_z=1/2 and S_z=-1/2) remains unchanged during the reaction; however, the polarization per radical increases. The spin system tends to re-establish the equilibrium due to the electron relaxation and cross-relaxation. The cross relaxation results in the formation of the net emissive CIDNP of the radicals, which is then transferred to the products.

Theoretical calculations, based on this model, well describe the kinetics of net CIDNP formation for different initial radical concentrations (Fig. 2).

A quantitative analysis of the kinetics and amplitude of the CIDNP effects allowed us to determine the time of the electron-nuclear cross-relaxation of the 2-hydroxy-2-propyl radicals.

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^{119}Sn CIDNP: CALCULATIONS AND EXPERIMENT

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Organotin chemistry is rather intensively developing field of research. However, CIDNP technique, that has been in a good practice when studying a number of the reactions of organometallic species of IV Group elements (Si, Ge), is less commonly used in the investigations of radical reactions of organotin compounds. Meanwhile, tin is a relatively convenient nucleus for NMR spectroscopy, and ^{119}Sn NMR has been also much studied [1]. This makes it possible to observe ^{119}Sn CIDNP effects, and not just the protons, as it is common for the reactions of organosilicon and -germanium compounds.

However, the most critical deterrent to these experiments is the absence of the rules for ^{119}Sn CIDNP analysis. Manfred Lehnig, a sole author published several papers on ^{119}Sn CIDNP [2], has already cast reasonable doubts on the applicability of S-T_0 approximation of radical pair (RP) theory to the analysis of ^{119}Sn CIDNP effects. These doubts are based on the extreme magnetic resonance parameters of tin-centered radicals, namely, ^{119}Sn HFI constants (nearly 200 times greater than usual ^{1}H values) and g-factors differing markedly from pure spin value.

The present report is devoted to exact calculations of net and multiplet ^{119}Sn CIDNP in arbitrary magnetic fields in the frames of diffusion approximation of the RP theory. Calculated values are employed for quantitative analysis of CIDNP formed in the photolysis of 2-methylpropanoyltripopyl-stannane, $Pr_3SnC(O)i\text{-}Pr$.

For the case of different RPs, it does makes sense to compare the contributions from S-T_0 and S-$T_{+,-}$ transitions to ^{119}Sn CIDNP formation in various magnetic fields. It would be expedient to consider the instances where Zeeman term is comparable with ^{119}Sn HFI as well as those with negligible ΔgH_0. Magnetic field dependencies of net and multiplet ^{119}Sn CIDNP were calculated for the RP with one tin-centered radical, $\Delta g = 1.55 \times 10^{-2}$ (RP-I), as well as for the RP comprised of two tin-centered radicals of identical structure, but with different isotopic composition (RP-II). It has been shown that S-T_0 transitions make a dominant contribution to net CIDNP formed in RP-I in high magnetic fields (those of modern NMR spectrometers). This is also true for multiplet CIDNP in the whole range of magnetic fields. At the same time net CIDNP in RP-II results from S-$T_{+,-}$ transitions. An important practical conclusion follows that one may employ Kaptein rules for CIDNP analysis in high magnetic fields for RPs where Zeeman term is comparable with HFI.

The report analyses ^{119}Sn CIDNP effects detected during the photolysis of $Pr_3SnC(O)i\text{-}Pr$. The results are compared with ^{1}H and ^{13}C CIDNP data.

The financial support of Russian Foundation for Basic Research (Grant No. 94-03-08975) is gratefully acknowledged.

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SPIN CHEMISTRY WITH d-ELECTRON RADICALS

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The principles of radical pair spin chemistry have been developed on the basis of investigations dealing with typical organic radicals where S is a good quantum number, i.e. spin-orbit coupling effects are weak, spin relaxation times are long, electron spin motion is governed by hpyerfine interaction, and reactivities of radical pair spin substates are subject to selection rules implying strict spin conservation in a chemical reaction step. All of these rules break down when dealing with radical pairs involving d-electron radicals with unpaired electrons localized at heavy atomic centers as is the case with many paramagnetic transition metal complexes.

As we have shown with a number of Ru^{III}-trisbipyridine type complexes, magnetic field effects can still be found with such systems, although at much higher fields than typically applied in the case of normal organic radical pairs. In this talk and a related poster we shall present new results on other d-electron systems. These involve ferrocenium ions obtained in radical pairs with methylene blue semiquinone by photooxidizing several ferroce derivatives in reactions with methylene blue triplets. Reacting an organic photosensitizer with a d-electron radical precursor seems to be a more widely applicable method than reactions utilizing photoexcited complexes, and can open access to the spin chemistry of many interesting new d-electron radicals.

Our experimental results serve as a basis to demonstrate some important concepts essential for generalizing the standard radical pair mechanism to the case of radical pairs involving d-electron radicals. The following features are essential:

- eigenstates of the *effective spin* should be used to account for the spin-orbit mixed nature of the d-electron radical
- in order to specify the reactivity of effective radical pair spin substates, these have to be projected to basis states of pure singlet and triplet spin.
- relaxation of the effective spin at the d-electron radical site must be explicitely taken into account.

Numerical solution procedures for the pertinent Stochastic Liouville Equation have been worked out for exponential as well as diffusional decay of the radical pairs (cf. symposium contribution by N.N.Lukzen). From a simulation of the experimental field dependence absolute values of the rate parameters of interest can be determined.

While such a quantitative analysis of magnetic field dependent kinetic effects is a new source from which values of the relaxation rate constants of the effective electron spin in the paramagnetic complexes can be obtained, we have also applied temperature dependent NMR measurements of ^1H and ^{13}C nuclear spin relaxation times to obtain independent confirmation of the spin chemically determined values and to use the temperature dependence for looking deeper into the mechanism of very fast electron spin relaxation of such $S_{eff} = 1/2$ Kramers systems in liquid solution.

THEORETICAL ANALYSIS OF IONIC STRENGTH AND MAGNETIC FIELD EFFECT ON GEMINATE RECOMBINATION OF COULOMB-REPULSIVE RADICAL PAIR RU(III)-COMPLEX/METHYLVIOLOGEN.

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The reactions of spin-correlated radical pairs(RP-s) wherein one of the radicals of the RP is d-electron transition metal complex (cf. symposium contribution by U.E.Steiner) are interesting in that despite a fast loss of spin correlation in RP owing to short relaxation time (10^{-11} -10^{-13} sec) of the spin of transition metal it is still possible to observe rather large magnetic field effects, although in magnetic fields significantly higher than usual (i.e. in the magnetic fields much higher than hfi constants).

Spin kinetics in these radical pairs is mainly determined by the short spin relaxation time of d-electron radical and (in high magnetic fields) by the large anisotropy of effective g-tensor and practically does not depend on hyperfine interactions and exchange interaction of radical spins. Due to this fact the number of parameters in the theoretical consideration of these reactions substantially decreases. For the theoretical description of magnetic field effects in these reactions a simple exponential model [1] was used assuming exponential kinetics of radical pair recombination from reactive spin states of RP in solvent cage and also exponential kinetics of radical pair cage escape. Though this model describes the main features of the process , it can be considered only as the first approximation since a number of characteristic properties of RP recombination in solutions such as existence of re-encounters of radicals and inter-radical distance dependence of the probability of recombination is not taken into account. Moreover, not all parameters of exponential model can be uniquely associated with molecular-kinetics parameters of a solvent and radical recombination probability parameters.

In the present paper the recombination reaction of RP $Ru(bpy)_3^{3+}$ (bpy = 2,2'-bipyridine) and methylviologen radical (1,1' dimethyl-4,4-bipyridinium radical cation; $MV^{\bullet+}$) was theoretically investigated on the basis of the numerical solution of a stochastic Liouville equation for spin density matrix of RP taking into account spin-relaxation, anisotropy of the g-factor of d-electron radical and also diffusional motion of radicals in mutual Coulomb repulsion field. The distribution of distances between radicals in RP-s at the moment of RP formation i.e. after electron transfer from the triplet exited state of $^*Ru(bpy)_3^{2+}$ on the MV^{2+} molecule was also taken into account.

Application of the magnetic field in this reaction results in the reduction of the fraction of radicals escaping into the solution bulk without recombination. The influence of magnetic-resonance parameters of radicals and kinetic parameters of media, including the ionic strength of solution, on magnetic field effects was investigated. The numerically simulated values of MFE-s were compared with experimental ones obtained by U.E.Steiner and co-authors.

Also the magnetic field effects in radical reaction involving ferrocenium ion radical and methylene blue semiquinone characterized by the absence of Coulomb interaction between radicals of RP were numerically investigated. From a comparison of our calculations and experimental data obtained by U.E.Steiner and co-authors the spin-relaxation time of ferrocenium ion-radical and parameters of recombination probability which was assumed exponentially decreasing with increasing of interradical distance were determined.

Acknowledgment The grant of an Alexander-von-Humboldt Foundation to N.L. is gratefully acknowledged.

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PHOTOCHEMICAL GENERATION OF IONS AND RADICALS IN LIQUID SOLUTIONS

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The bimolecular electron transfer followed light excitation of electron donor D or acceptor A proceeds according to the kinetic scheme

$$D + A^* \Longrightarrow [D^+ ... A^-], \qquad (1)$$

Then ion-radicals may either recombine or go away and be detected by FT-EPR [1]:

$$[D...A] \Longleftarrow [D^+ ... A^-] \Longrightarrow D^+ + A^-. \qquad (2)$$

The shape and the magnitude of position dependent rates of forward and backward electron transfer were analyzed with account of vibronic excitations of reaction products. The initial distribution of photogenerated ions was studied and the mean inter-ion distance was shown to increase non-monotonously with the free energy of ionization.

The separation quantum yield of ion-radicals was studied within the unified theory of photoionization followed by geminate recombination [2]. The yield remains negligible with increase of ionization free energy until ions are created inside the recombination zone (kept fixed) and increases rapidly when the start is taken outside. This alternative is also responsible for an essential violation of Marcus' free energy gap law at slow diffusion.

In non-polar solvents the generation of neutral radicals from $D = BH$ occurs if proton tunneling dominates over backward electron transfer [1]:

$$D^{\cdot} + AH^{\cdot} \Longleftarrow [D^{\cdot} ... AH^{\cdot}] \leftarrow [BH^+ ... A^-] \Longrightarrow BH^+ + A^-. \qquad (3)$$

The theory describes not only the build-up of radicals but their distribution over distances as well. The latter is expanding with time so that dipole-dipole broadening decreases resulting in better resolution of superfine structure.

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EFFECTS OF HIGH MAGNETIC FIELD UPON CHEMICAL REACTIONS

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Recently, the effects of high magnetic fields on chemical reactions have received increased experimental and theoretical attention [1]. In this paper, we have studied the effects of high magnetic field ($\leq$8T) on deposition of metals and crystal growth of diamagnetic compounds.

(1) Deposition of Copper Metal from Aqueous Solution

In a plastic vessel, a zinc wire (5 ϕ x 250 mm) was placed on a piece of filter paper (40 mm x 300 mm) wet with a copper chloride solution. The vessel was then placed inside the bore tube (50 ϕ x 375 mm) of a superconducting magnet. At zero field, deposition of copper metal occurs uniformly around the wire (fig.1a). When magnetic fields (5 and 8 T) are applied, it occurs mainly at the center part of the wire (fig. 1b,c).

The above-mentioned reaction is given by the following equation,

$$Cu^{2+} + Zn \rightarrow Cu\downarrow + Zn^{2+} \quad (1)$$

Because of the order of ionization tendency, copper metal deposits from a copper chloride solution, when a zinc wire is dipped in the solution. The results can be interpreted in terms of the magnetic forces F_{GMF} on the ions intervened in the reaction,

$$F_{GMF} = (\chi/\mu_0)B(z)dB(z)/dz \quad (2)$$

where χ is the magnetic susceptibility of ion, μ_0 is the magnetic permeability, $B(z)$ is the magnetic field strength at the position z, and $dB(z)/dz$. is the magnetic field gradient at z. A paramagnetic ion (Cu^{2+}, $\chi = +1300 \times 10^{-6}$ cm^3 mol^{-1}) is attracted strongly by the magnetic force F_{GMF}, whereas a diamagnetic ion (Zn^{2+}, $\chi = -7 \times 10^{-6}$ cm^3 mol^{-1}) is repelled by the field. This results in the localized deposition of copper metal in a gradient magnetic field. Analogous effects are observed in the deposition of silver metal [2].

(2) Crystal Growth of Diamagnetic Compounds

Benzophenone is crystallized from a hot hexane solution. At zero field, white needles (10-30 mm in length) of benzophenone deposit randomly. In the presence of a magnetic field (8T), the needles are orientated in such a way that the long axis of the needles is perpendicular to the magnetic field (fig. 2). In the crystallization of potassium chlorate, it precipitates as white crystals in the form of flat plates (ca. 5 mm x 5 mm x 0.1 mm), which are randomly orientated at zero field. In the presence of a magnetic field (8T), the plates are orientated in such a way that the normal of the plates is parallel to the magnetic field. Magnetic orientation of diamagnetic crystals is mostly attributable to the anisotropy of their diamagnetic susceptibilities. The phenomena mentioned above seem to commonly occur when crystals have large anisotropic diamagnetic susceptibilities.

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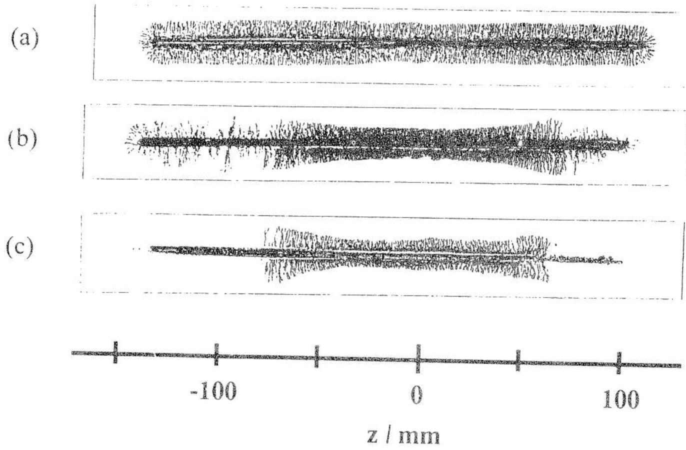

Fig. 1. Magnetic field effects on copper deposition. (a) 0 T, (b) 5 T, (c) 8 T

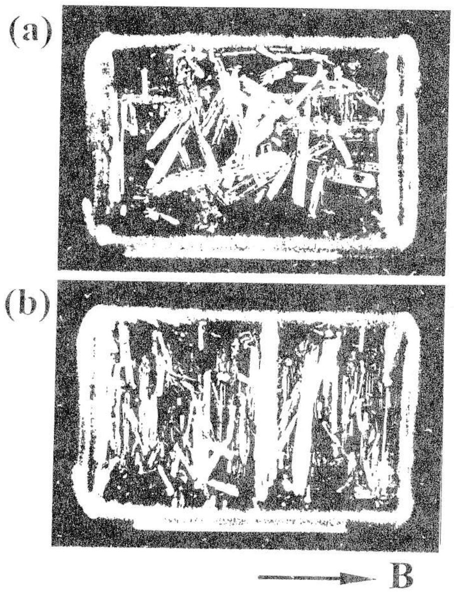

Fig. 2. Magnetic orientation of benzophenone crystal. (a) 0 T, (b) 8 T.

UNRAVELLING MULTI-CHANNEL PHOTO-INDUCED REACTIONS WITH FT-EPR

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In the past five years, Fourier-transform EPR (FT-EPR) has seen a tremendous increase in applications. FT-EPR seems to be well suited for investigations of photo-induced charge transfer reactions in solution. By combining its inherent high time and frequency resolution, different reaction intermediates can be identified unambigously.

This capability is especially important, if the electronically excited species can react not only with substrate molecules but also with the solvent. Such competing reaction channels can only be analyzed, if the EPR intensity of all paramagnetic reaction products can be measured over several decades in time.

We have studied in detail a photo-induced hydrogen abstraction reaction in the system Anthraquinone (AQ)/di-tert.-butylphenol/isopropanol. Here the metastable triplet state ^3AQ can abstract an H-atom either from the phenol or from the α carbon of the solvent molecule. By selective deuteration of phenol and solvent molecules, respectively, we studied the kinetic isotope effect of both reactions. We could demonstrate that the hydrogen abstraction from the phenol occurs via a consecutive electron/proton transfer. In the first step, a radical ion pair is generated. The subsequent mass transfer apparently is controlled mainly by the relative arrangement of both ions, as indicated by a vanishing isotope effect.

The absence of an isotope effect is documented by a determination of the ratio of neutral (9)-hydroxy-anthroxyl radical to anthraquinone radical anion signal intensities within the first 100 ns after the laser flash. This intensity ratio is a measure for the proton abstraction rate compared with the escape rate of the anion from the solvent-stabilized radical ion pair.

In the second reaction channel, the photo-excited ^3AQ abstracts a hydrogen atom from 2-propanol leading to formation of (9)-hydroxy-anthroxyl radicals as well as neutral radicals. The rather slow reaction constant of $2 \times 10^7 M^{-1} S^{-1}$ indicates that this step cannot be diffusion-controlled but rather proceeds via an activated step.

By comparing the initial signal build-up with that of the "instantaneously" generated triplet state of [60]-Fullerene, we measured a delay of approximately 10 to 20 ns for the observability of the propan-(2)-ol-(2)-yl radicals, in accordance with the proposed reaction scheme, which also includes final separation of the solvent-correlated neutral radical pair.

Including various spin polarization mechanisms, a complete reaction scheme is derived, from which the time profile of all radicals involved can be calculated.

PHOTOIONIZATION IN MICELLAR SOLUTIONS: A FOURIER TRANSFORM EPR STUDY

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Fourier Transform EPR (FT-EPR) has been used to study the mechanism and kinetics of photoionization of phenothiazine (PTH) in homogeneous and micellar solutions. The formation and decay of paramagnetic species generated by pulsed-laser excitation of PTH was monitored with nanosecond time resolution. The investigation focused on how the time profiles of the resonances of the primary radicals formed in the reaction

$$\mathrm{PTH} \xrightarrow{\text{light}} \mathrm{PTH}^{+} + e^{-}_{sol}$$

are affected by the solvent medium. The study also was concerned with medium effects on the reaction of the solvated electron with electron acceptors

$$e^{-}_{sol} + \mathrm{A} \rightarrow \mathrm{A}^{-}$$

It was found that a change from homogeneous solution to micellar solution has a pronounced influence on Chemically Induced Dynamic Electron Polarization (CIDEP). This is attributed to the compartmentalization of reactants and products in micellar media. Relaxation characteristics of the paramagnetic species also exhibit a solvent medium dependence and this is used to get a better understanding of the spatial distribution of solutes in micro-heterogeneous media.

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Investigation of photogenerated radical ions of benzophenone derivatives by spin polarization effects detected by time resolved Fourier Transform EPR

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The photophysical and photochemical reaction pathways of aromatic ketones and quinones are dominated by the singulet-triplet intersystem crossing with a strong spin-polarization mechanism. In alcoholic solutions and in the presence of amines the prefered triplet deactivation reactions are electron transfer reactions and / or hydrogen abstraction from the solvent or from the amine ground state molecules. Regarding the general reaction scheme with different benzophenone carboxylic acid derivatives as photoactivated molecules the biphotonic ionization, the electron transfer reaction with different secondary and tertiary amines and the interactions in solvent stabilized radical ion pairs were studied.

With high laser photon fluxes the biphotonic ionization dominates the photochemical behaviour of benzophenone substituted with carboxylic acid groups in different positions. Whereas the emissive spin-polarized photoelectrons disappear by an addition reaction to ground state benzophenones the different benzophenone radical cations decay by nucleophilic addition of OH^- to the aromatic ring generating cyclohexadienyl radicals, and by β-scission of the intermediate alkoxy radicals produced by OH^- additon to the mesomeric cationic keto group. The decay channels of those radical cations depend strongly on the positions of the carboxylic acid substituent. The product radicals of this β-scission are various aryl radicals or phenyl radicals depending on the position of carboxylic acid positions.

The photoreduction of the spin-polarized benzophenone triplets by different amines generates radical ion pairs with different amount of triplet and/or radical pair polarization. The kinetics of the radical ion pairs, the mechanisms of different secondary reactions and the relaxation behaviour of radical anions and radical cations will be discussed in various polar solvents like alcohols and water. With low amine concentration the lifetimes of the benzophenone triplets are in the microsecond range. In this case the radical-triplet pair mechanism in the free radicals could be detected.

QUANTUM OSCILLATIONS IN RADIO-LUMINESCENCE AND PRIMARY SPUR PROCESSES IN HYDROCARBONS

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The review will be presented of our recent investigations of fast spur reactions in irradiated alkanes by the quantum beats technique. The quantum beats have been observed in the recombination of singlet-born spin correlated radical ion pairs $(DPS)^+/(PTP)^-$, formed by scavenging of solvent holes (S^+) and free electrons with diphenylsulfide-d_{10} (DPS) and *p*-terphenyl-d_{14} (PTP) molecules, respectively. The singlet-triplet oscillations in these pairs are induced by the difference in cation and anion g-factors [1].

The phase shift of quantum oscillations has been observed for low concentrations (10^{-2} M) of DPS [2]. The shift results from the delay in the $(DPS)^+$ formation in the course of reaction

$$DPS + S^+ \rightarrow DPS^+ + S$$

The rate constants of hole trapping have been obtained for DPS and other acceptors from the concentration dependencies of the phase shift. The rate constants have been found to substantially exceed the diffusion controlled ones for cyclic alkanes, *iso*-octane and squalane [3].

At higher DPS concentrations, when S^+ transforms to DPH^+ very quickly, the fraction of singlet spin-correlated pairs in radiation track has been obtained from the amplitude of oscillations. For fast electrons the fraction is in the range of 0.54 to 0.36 for different alkanes [4], while for X-rays with a higher track density and the larger probability of cross recombination it is two times smaller [5].

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ODESR AND MARY STUDIES OF TRANS-DECALIN RADICAL CATION.

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Optically Detected ESR (OD ESR) has become a powerful tool for studying short-lived spin-correlated radical ion pairs forming in nonpolar solutions under ionizing radiation. Using this technique the signals of cation radicals of *trans*-decalin were observed in alkane solutions at cryogenic temperatures (Fig. 1). These signals were found to vanish and disappear when temperature grows, that was previously attributed to reaction of deprotonation [1]:

$$\mathrm{RH}^{\cdot +} + \mathrm{RH} \longrightarrow \mathrm{R}^{\cdot} + \mathrm{RH}_2^{+}. \qquad (1)$$

The study of magnetic field effects on reaction yield (MARY-spectroscopy) of chemical reactions also provides valuable information on short-lived spin-correlated radical pairs. As was recently demonstrated, the coherent nature of radical ion pairs can result in the appearance of additional local fluorescence intensity maxima at level-crossing fields [2]. This phenomenon opens possibilities for identification of short-lived paramagnetic species and studying of reactions they are involved in.

The breaking down of initial spin coherence in the course of dynamic transitions between two nearly degenerate molecular states of *trans*-decalin $^2\mathrm{A_G} \leftrightarrow {}^2\mathrm{B_G}$ [3] should lead to broadening of narrow MARY-spectrum lines, which allows extracting quantitive information on the rate of this process. In the present work this technique was employed to demonstrate that for radicals cation of *trans*-decalin the intramolecular transitions take place, which results in electron spin relaxation. Calculated within the frame of this model ODESR and MARY spectra are in good agreement with experimentally observed ones (Fig. 1).

The ability of *trans*-decalin radical cations (holes) to take part in positive charge hopping was widely debated. Very fast hole hopping was proposed to explain the conductivity measurements in cyclic hydrocarbons [4], but this explanation was questioned taking into consideration the fate of radical cation (reaction 1) in subsequent publications [1], since, unfortunately, there were no direct proofs for existence of (*trans*-decalin)$^+$ at room temperatures. Therefore, this work presents first direct spectroscopic evidence of *trans*-decalin radical cation stability in nanosecond timescale.

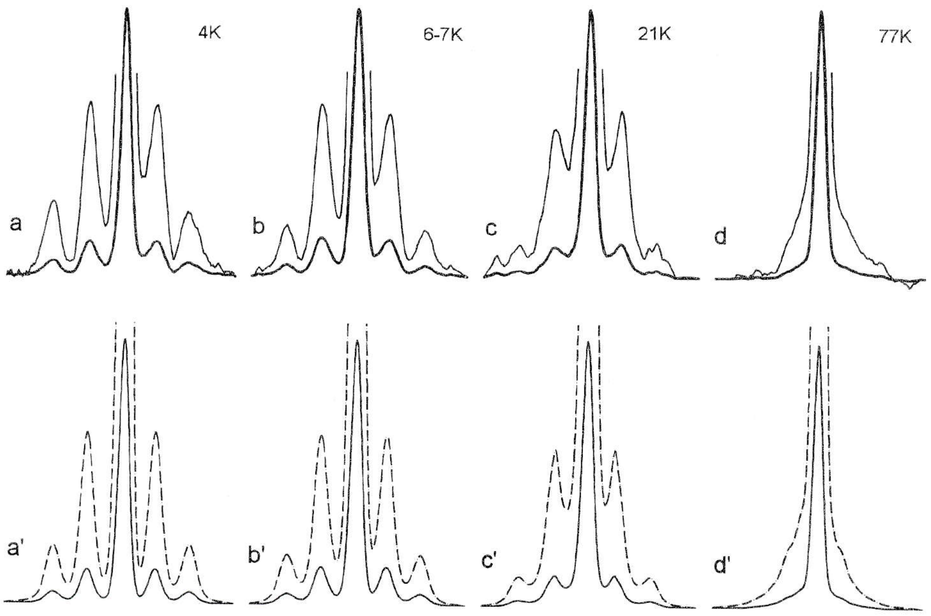

Figure 1: ODESR spectra of 0.3 M *trans*-decalin in squalane matrix at different temperatures. (a–d) experiment; (a′–d′) calculated within the frame of two-state exchange: (a′) $k_{AB}=10^8$ s^{-1}, $k_{BA}=5\times10^9$ s^{-1}, $T_1=8$ μs; (b′) $k_{AB}=10^8$ s^{-1}, $k_{BA}=1{,}25\times 10^9$ s^{-1}, $T_1=2$ μs; (c′) $k_{AB}=1{,}7\times10^8$ s^{-1}, $k_{BA}=3{,}3\times10^8$ s^{-1}, $T_1=1$ μs; (d′) $k_{AB}=10^9$ s^{-1}, $k_{BA}=10^9$ s^{-1}, $T_1=0{,}1$ μs.

Acknowledgement. This work was performed under the auspices of INTAS Grant #93–1626.

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Spin-Orbit Coupling Induced Electron Spin Polarization

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Recently, we proposed a new electron spin polarization mechanism, spin-orbit coupling mechanism(SOCM), due to heavy atoms.[1,2] When photosensitizers contain heavy atoms, net polarization can be created by SOC interaction. Unusual net-absorptive CIDEP spectra were observed in xanthene dye sensitized photoinduced electron transfer reactions. The enhancement factor of the transient signals increases with increasing atomic number of the halogen in the sensitizer. In contrast, the radical yield remarkably decreases with increasing heavy atoms. In this paper, we present the effects of the heavy atom containing in the donor molecules which are not directly excited by photolysis. Echo detected FT-EPR spectra were measured for the radicals generated from the photoexcitation of duroquinone (DQ) in the presence of *N,N*-dimethylaniline (DMA) and its mono-halogen substituents.

FT-EPR measurements were carried out using an X-band pulsed EPR spectrometer (Bruker ESP 380E) equipped with a dielectric resonator at room temperature. A Nd:YAG laser was used as the light pulse source. The sample solution was deoxygenated by argon gas bubbling before and during the measurements, and was flowed into a quartz cell within the EPR cavity.

When DMA and 4-chloro-DMA were used as the electron donor, the net-emissive polarization due to triplet mechanism was observed. In contrast, the electron donor of 4-bromo-DMA and 4-iodo-DMA gave unusual net-absorptive CIDEP spectra of the DQ anion radical at the delay time of 200 ns between the laser and first microwave pulses. The net-absorptive polarization observed is attributable to spin-orbit coupling mechanism (SOCM).

Dependence of the enhancement factor of the spin polarization on the halogen substituted position also has been examined. When 2-bromo-DMA and 4-bromo-DMA were used as the electron donor, net absorptive CIDEP spectra were obtained. In contrast, the donor of 3-bromo-DMA gave net-emissive polarization.

The present results indicate that the CIDEP spectra of the acceptor anion radical are remarkably affected by the heavy atom of the donor cation radical. The net absorptive polarization observed suggests that the preferential selectivity in the triplet sublevels of the contact radical pair is induced for the back electron transfer by the heavy atoms of the donor. One-centered SOC interaction plays an important role to induce the simultaneous changes of the orbital angular and spin operators, because direct SOC interaction decreases sharply as the distance of pair radicals increases.

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Magnetic Field Effects on Photoinduced Electron Transfer Reactions between Carbonyl Compounds and Anilines in Non-Viscous Homogeneous Solutions

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Magnetic field effects (MFEs) on dynamic behavior of radical pairs have been studied extensively, but most of the MFEs on the radical pair dynamics have been observed in confined system such as micellar solutions and viscous solutions. Furthermore, almost all of rare exceptions in non-viscous solutions have been carried out under smaller magnetic fields than 0.3T. Therefore, we have started to study the MFEs on the photochemical reactions in non-viscous homogeneous solutions at room temperature(293K) by a nanosecond laser flash photolysis under magnetic fields (B) of 0-10T.

We have found the MFEs on the time profiles of the transient absorption ($A(t)$) in the photoreactions of xanthone (XO) and 2,5-dimethyl-p-benzoquinone (Q) with N,N-diethylaniline (DEA) at room temperature in 2-propanol [1]. In the reaction of XO with N,N-diethylaniline (DEA) in 2-propanol (ε=19.9, η=2.4 cP), a triplet radical ion pair between XO anion radical ($XO^{\cdot -}$) and DEA cation radical ($DEA^{\cdot +}$) was generated by an electron transfer from DEA to excited triplet XO and this radical ion pair showed fairly large MFEs. The yield of the escaped $DEA^{\cdot +}$ increases with increasing B from 0 to 1.5T, but decreases from 3 to 10T[1]. In the reaction of XO with N,N-dimethylaniline (DMA), the reverted MFE was also observed in 2-propanol.

The $A(t)$ curves were also measured in the reactions of XO with DEA in several solvents. In the reactions in less polar solvents than 2-propanol such as benzene (ε=2.28), *n*-hexane(ε=1.89), cyclohexane(ε=2.02), and 2-methyl-2-propanol(ε=12.5), hydrogen abstractions were found to occur and the generated neutral radical pairs showed no MFE. On the other hand, electron transfers were found to occur in the reactions in acetonitrile(ε=37.5, η=0.36 cP) and water(ε=80.2, η=1.0 cP)-acetonitrile mixture and the generated radical ion pair showed MFEs. These MFEs, however, were smaller than that in 2-propanol. This is because the escapes of radicals from radical pairs in acetonitrile and water-acetonitrile mixture are much faster than that in 2-propanol for the following reasons. (1) Since the dielectric constants of acetonitrile and water are much larger than that of 2-propanol, the Coulombic interaction in radical ion pairs in acetonitrile and water-acetonitrile mixture is much weaker than that in 2-propanol. (2) The viscosity of acetonitrile and water are lower than that of 2-propanol.

The reverted MFEs on the $A(t)$ curves were also observed in the photoreactions of Q with DEA in 2-propanol. The yield of the escaped aniline cation radicals increased with increasing B from 0 to 0.1T, and then decreased with increasing B from 1.5 to 10T. The reversion of the MFEs observed in this reaction is larger than that in the reaction of XO[1]. The reverted MFE was also observed in the reaction of XO with DMA in 2-propanol. Such reverted MFEs can be explained by the relaxation mechanism[2,3] and/or a combination of the hyperfine coupling mechanism and the Δg mechanism[2]. The mechanism of these MFEs observed in non-viscous homogeneous solutions will be discussed in detail.

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MAGNETIC FIELD EFFECTS OF MULTI-NUCLEI SYSTEMS

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Recently we have been able to perform numerical calculations of magnetic field effects (MFEs) for several realistic radical pair (RP) systems. Multi-nuclei RPs with and without relaxation have been treated. Some hitherto unobserved spikes in the yield versus magnetic field curves have been found, and we have been able to quantify the effect of intraradical relaxation.

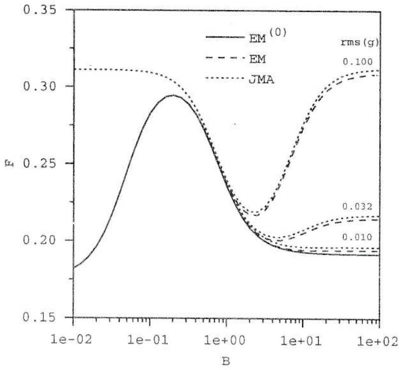
Except for high fields such calculations are extremely demanding, and both computer memory and computer time becomes a limiting factor. Furthermore numerical errors can be overwhelming if one is not careful. The problems arise from the dimensions of the matrices involved in the calculations. The dimension of the spin part is equal to 16×4^n for n spin one half nuclei, and thus for a radical pair (RP) with a single spin one half nucleus the size of the spin matrices is 64×64. The dimension of the diffusion matrix is equal to the number of discretization points, e.g. 100. The dimension of the total problem is the product of the two, i.e. 6400×6400 for the above system. The task is therefore to reduce the dimensions of both parts as much as possible.

Our numerical calculations are based on the backward Stochastic Liouville formalism [1] which is particular convenient because it allows a direct and simultaneous calculation of all observables of interest. An extra advantage is that the average value of the desired quantity is obtained as a solution that contains the complete dependence on the separation and spin state of the initial RP. As in the Pedersen-Freed work [2] the spatial variable is discretized but in order to cover the space more efficiently by a small number of points we use a transformed variable z which is discretized equidistantly. For many applications the free diffusion transformation $z = 1/x$ is useful or even optimal; $x = r/d$ is the dimensionless separation of the radicals measured in units of the distance of closest approach d. For RPs in an unrestricted volume it is possible to incorporate the analytically known asymptotic solution into the numerical method. Thereby the number of discretization points can be reduced to 10 or even less [3].

Multi-nuclei systems without relaxation can be treated exactly by decomposing the spin blocks into smaller blocks by use of symmetry arguments. In a static magnetic field the z-component of the total spin $\mathbf{F}$ is conserved. Thus for a RP with 2 non-equivalent spin one half nuclei the spin matrices automatically decomposes into 5 smaller matrices corresponding to $F_z = -2, -1, 0, +1, +2$. For identical nuclei further reductions are possible. The principles behind this reduction is quite simple but the actual implementation into a useful algorithm is difficult. As a result of this simplification scheme it is possible to calculate MFEs exactly for systems with 4 or less non-identical, any number of identical, or 2 non-identical plus any number of identical nuclei. If the RP is confined in space, e.g. to the interior of a micelle, then much larger systems can be treated by use of the Johnson-Merrifield approximation (JMA) [5].

Multi-nuclei systems with relaxation can only be treated exactly for special cases. One obvious case is a high field system without cross-relaxation. Fortunately, relaxation is most important for RPs confined to a restricted volume, e.g. micellar systems. For such systems the exponential model (EM) and its supercage extension are applicable [5]. In the EM there is no spatial dependence of the Liouville operator and the dimension of the problem is therefore solely determined by the size of the spin matrices which, however, can still be rather large. The EM can handle 3 non-equivalent nuclei or any number of equivalent nuclei. We have shown [6] that the EM can be approximated by the JMA for almost all field values. The latter approximation allows up to 8 non-equivalent nuclei to be treated. Note, however, that the more accurate supercage JMA is limited by the first (geminate) stage.

The figure shows the effect of relaxation due to Δg anisotropy on the recombination probability F of a RP in a micelle. The unit of the magnetic field corresponds to 20 G and the rms(g) value indicated on the figure is the root mean square value of the g-tensor anisotropy. For comparison the results of a calculation using the EM without relaxation is given by the full line.



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EFFECTS OF MICELLAR SIZE ON THE ESR SPECTRA OF SPIN-CORRELATED RADICAL PAIRS WITH VERY LARGE HYPERFINE COUPLING CONSTANTS (^{13}C AND ^{31}P)

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Spin-correlated micellized radical pairs (SC RP) with large hyperfine coupling constants exhibit wide antiphase structures (APS) in their ESR spectra (Figs. 1, 2 and Table 1). This feature allowed us [1] to separate the ESR signals between SC RP and free (escaped) radicals (Fig.1) and to study the line shape of APS in some detail. By a convenient choice of the pair, we were also able to observe the effect of flip-flop electron-nuclei transitions on the shape of APS (Fig.2). Such transitions become important when the stay of geminate SC RPs inside the rather viscous micellar core is relatively long.

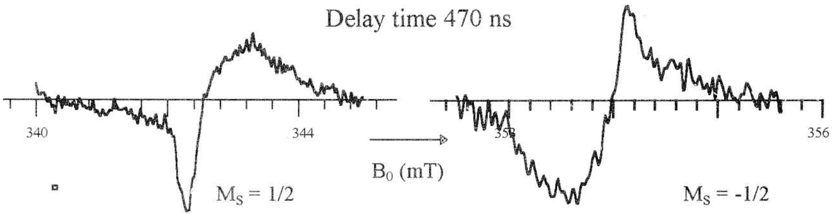

Fig.1 SC RP of ^{13}C-benzoyl and sec phenethyl radicals (System 1) in C_{10} micelle.

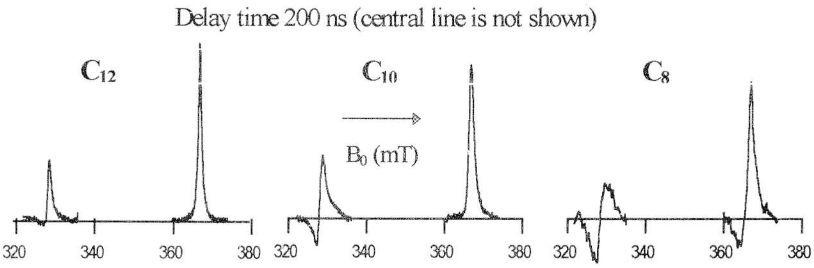

Fig.2 SC RP of diphenyl phosphonyl and 2,4,6-trimethyl benzoyl radicals (System 2).

SC RPs were generated in 308 nm laser photolysis of ^{13}C-labelled α-methyldeoxybenzoin (system 1) and 2,4,6-trimethylbenzoyl diphenylphosphine oxide (system 2) in sodium (8-12) alkylsulfate micelles. System 1 is a triplet-correlated pair of ^{13}C-labelled benzoyl ($A[^{13}CO]=12.7$ mT) and sec-phenethyl radicals. System 2 is a pair [2] of 2,4,6-trimethylbenzoyl and diphenyl phosphonyl radicals (A[^{31}P]=38.3 mT) formed in photodissociation of the triplet parent ketone. Both of these pairs exhibit well resolved APS (Fig. 1 and 2) whose width, asymmetry, and splitting parameter depend on the micellar size (Table 1). APS values only of low field line, M_s=1/2, of the System 2 are presented in the Table. These values slightly depend on the short delay time. The given data correspond to the 400 ns delay.

N	Antiphase splitting (mT)	
	System1	System 2
12	0.96 ±0.05	0.85 ±0.04
11	1.02 ±0.05	1.19 ±0.04
10	1.54 ±0.06	1.60 ±0.04
9		2.05 ±0.04
8		2.47 ±0.06

In the ^{13}C system, the SC- and ST_0 RPM polarized radicals can be observed simultaneously at any delay time. The ST_0 polarization is from the escaped ^{13}C-benzoyl radicals which retain spin coherence formed inside the micelles. The width of the ESR lines from these radicals is much narrower than the width of corresponding APS lines. In large micelles, the APS splitting is shown to be wholly determined by the rate of electron spin exchange relaxation. A static splitting due to a non-zero average exchange potential was found in small micelles, in which the APS lines are markedly asymmetrical. This asymmetry is caused by the difference in spin-exchange effects on the rates of S- and T- correlated ESR transitions, by the effects of spin-selective chemical reaction, and fast equilibration of the population of the corresponding spin-levels. All of these features were simulated by numerical integration of the Stochastic Liouville equation for SC RP in the resonance microwave field; supercage model was used to simulate the diffusion motion of radical partners inside the micellar interior.

In the ^{31}P system, the ESR spectra from SC RP cannot be simulated within the high-field approximation. Numerical analyses indicates that two kinds of flip-flop transitions are operative in this system (type-I and type-II). Type-I transitions (ST_+ as well ST_-) occur in the regions where the exchange potential between the radical partners are negligible and result in the polarization pattern which is very similar to that of RPM; type-II transitions are induced by adiabatic passage of the radicals through the region of $S\beta$–$T\alpha$ crossing. The latter transitions cause rapid equilibration of the initial population between the corresponding spin states. Type-I transitions are more efficient in larger micelles at the conditions of diffusion controlled reaction, while type-II transitions are prevalent in smaller micelles.

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Magnetic Field Dependence of CIDEP: Spin-Correlated Radical Pairs

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We have investigated magnetic field dependence of the CIDEP spectra of spin-correlated radical pairs (SCRP) in various systems using cw time-resolved EPR spectrometers in the X, S and L bands. The systems studied include acetone-d_6 in 2-propanol-d_8, xanthone (Xn) and 2,6-di-t-butylphenol (DBP) in a sodium dodecylsulfate (SDS) micellar solution, and zinc tetra(4-sulfonatophenyl) porphyrin (ZnTPPS) and p-benzoquinone (p-BQ) in a cetyltrimethylammonium chloride (CTAC) micellar solution. The CIDEP spectra of the SCRP produced by the photolysis of these systems are examined at X, S and L bands.

In the case of acetone-d_6 a characteristic SCRP spectrum with E/A type hyperfine lines become dominant at very low temperatures (< - 80°C) in the X band. However, the SCRP signals are much weaker in the S and L band spectra; the E/A lines can only be observed in the central hyperhine line even at very low temperatures.Thus the result seems to indicate that the intensity of the SCRP signal decreases strongly with a decrease of the magnetic field. It is likely that weaker signal intensities at lower magnetic fields are due to shorter spin-lattice relaxation times (T_1) that are caused by the rotational motion and / or the fluctuations of the exchange and dipolar interactions. In the fast rotation (fluctuation) limit, T_1 is independent of the strength of the magnetic field, but in the slow limit T_1 decreases with decreasing the external magnetic field. The observed result can be explained in terms of the slow rotation (fluctuation) of the SCRP which are believed to be trapped in a rigid solvent structutre.

The CIDEP spectrum of the Xn / DBP in SDS system in the X band shows a characteristic E/A/E/A pattern due to the SCRP with an additional net emissive polarization. At lower microwve frequencies the net emiissive component decreases and it is not observable in the L band. This emissive component is assigned to the polarization due to TM. The magnetic field dependence of TM studied in a previous work indicates that such dependence is expected when the rotational correlation time of triplet xanthone is shorter than 10^{-9}s. The E/A/E/A SCRP spectrum, on the other hand, scarecely changes with the microwave frequency, or the magnetic field strength. The decays of the SCRP signals at 0 °C in the X and L bands are expressed by single exponentials with decay times of about 3 and 2 μs in the X and L bands, respectively. This indicates that the spin-lattice relaxation time decreases somewhat on going from the X band to the L band, but the system is not in the slow motion limit and the correlation time is on the order of 10^{-11}s. This correlation time appears to be too short for the rotation of the SCRP in a micellar solution.

The CIDEP spectrum of ZnTPPS / p-BQ in CTAC in the X band consists of the spectrum of the SCRP and that of $ZnTPPS^{3-}$, but in the S and L bands only the SCRP spectrum is observed. In the S and L bands distortions due to TM and RPM(Δg) become less significant making the spectrum symmetric.

Analysis of CIDEP spectra of spin correlated radical pairs. Quasistatic and short correlation time approximations

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The quasistatic (QSA) and short correlation time (SCTA) approximations are very well known in the general relaxation theory and, in particular, in the theory of magnetic resonance [1]. They enable one to describe quite easily the complicated relaxation processes in multispin systems. The theory of magnetic field effects (MFE) in liquid phase chemical reactions is a part of the magnetic resonance theory and, therefore, QSA and SCTA are expected to be very useful in studying MFE. Surprisingly, no analysis of QSA and SCTA as applied to MFE has been made so far. SCTA is of special importance for the MFE theory because, as will be shown, the majority of MFE can be described in different variants of this approximation.

This lecture concerns discussion and *interpretation* of some known results of theoretical and experimental investigations of MFEs in terms of QSA and SCTA. The main attention will be paid to analysis of CIDEP spectra of spin-correlated radical pairs (RPs) although the results of the analysis are quite general and can be applied to other MFEs as well.

The main difficulty in application of QSA and SCTA to MFEs results from fact that the simple formulation of these approximations is possible only if there is the well defined fluctuation time of stochastic Interactions that induce relaxation. As to fluctuations of interactions which are responsible for MFEs in chemical reactions in liquids, they are caused by stochastic relative motion of reacting particles and are typically described by many different times. It can be shown, however, that in this situation it is still possible to interpret the results in terms similar to those used in QSA and SCTA.

Analysis will be based on analytical solutions of the stochastic Liouville equation (SLE) which have recently been derived in [2] and [3] in the sudden perturbation (SPA) and nearly adiabatic (NAA) approximations, respectively. The parameter that controls these approximations is the generalized Messey parameter

$$\xi = \sqrt{Q/D\alpha^2} \tag{1}$$

where Q is the characteristic frequency of the spin Hamiltonian, D is the diffusion coefficient and α^{-1} is the characteristic scale of the exponential distance dependence of the exchange interaction. Namely, SPA and NAA correspond to $\xi \langle 1$ and $\xi \rangle 1$, respectively.

SPA ($\xi \langle 1$) will be shown to be the analog of SCTA for diffusion controlled processes although this analogy is fairly tricky because of very slow, power type decay of correlations of diffusion controlled fluctuations. In SPA within the accuracy $\prec \xi^2$ the effects of short range interactions (reactivity, exchange interaction, etc.) are described by the corresponding radii: reaction and generalized relaxation radii for diagonal and nondiagonal elements of the spin density matrix, respectively. The approximation of effective radii enables one to easily calculate all kinds of MFEs and, in particular, the CIDEP spectra. In the case of CIDEP spectra the parameter Q in eq.(1) is either a splitting of lines (coherent parameter ξ_c) or a linewidth (relaxation parameter ξ_r) The close relation between SPA and SCTA and its manifestation in the

CIDEP spectra, will be illustrated by a few simple model and more complicated realistic examples (free diffusion of radicals, biradicals, RP in micelles, etc.) The important role of other parameters

$$\xi = \sqrt{Qd^2 / D} \text{ and } \gamma = \sqrt{QR^2 / D} \qquad (2)$$

where d is the distance of closest approach and R is the characteristic size of cage (in the presence of the cage), is also discussed. They will be shown to govern the substantial changes of the MFE generation kinetics and, in particular, kinetics of CIDEP generation. The parameter ξ controls the first reencounter approximation [2] (valid for $\xi < 1$) while the parameter γ governs the transfer from cage approximation to the supercage one [4]. Some changes in CIDEP spectra are also predicted.

NAA (with $\xi_c > 1$, where in ξ the parameter Q is the splitting of terms) appears to approximately correspond to QSA. In NAA the population relaxation (which is nonadiabatic in NAA) decouples from the phase relaxation. Within NAA the validity of QSA for the CIDEP line shape is determined by the inequality $\xi_r > 1$, where ξ_r is defined by eq.(1) with Q being the linewidth. If the linewidth is smaller than the line splitting, in NAA the opposite case $\xi_c < 1$ is still possible. This case corresponds to SCTA.

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Dynamic Effects in EPR Spectra of Spin–Correlated Radical Pairs and Biradicals. Experiment and Theory

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Radical pairs (RPs) produced by photolysis of photochemically active, amphiphiles were observed using time–resolved electron paramagnetic resonance (TREPR) spectroscopy. After the Norrish I cleavage reaction, both radicals retain surfactant character and thus remain as part of the micelle with their radical centers at the end of a C_{11} or C_{12} surfactant chain. The time evolution of the EPR signal is unusual in that the radical pair mechanism (RPM) of chemically induced dynamic electron spin polarization appears at the very earliest delay times (0.1 to 1.0 &s), whereas the expected polarization pattern from the spin–correlated radical pair (SCRP) mechanism is only seen at later delay times (> 1 &s). This is the opposite of what has been observed previously for RPs produced by hydrogen atom abstraction using photoexcited triplet molecules dissolved in micelles. It is suggested that the phenomenon arises because tumbling and diffusion of the RPs is slow in the micelle interior. The result is a magnetic resonance dynamic effect that favors the appearance of the RPM polarization over the SCRP type until later delay times. The role of this dynamic effect in the appearance of both polarization mechanisms will be qualitatively discussed.

The X–band (TREPR) spectra of 1,16– and 1,21– acyl–alkyl biradicals, obtained in toluene solution at low temperatures (193 to 253 K), will also be presented. The spectra show a strong temperature dependence in their patterns of chemically induced electron spin polarization. The SCRP mechanism dominates at high temperatures, while the RPM is the main pattern at lower temperatures. It is postulated that the SCRP spectrum disappears at the lower temperature due to modulation of the exchange interaction (J) between the unpaired electrons. Simultaneously the RPM is enhanced by this motion. Values of J calculated from static end–to–end distance

distributions for the C_{21} biradical show that in the absence of this dynamic effect, an intense SCRP spectrum would be present at the lower temperature. The results demonstrate that the interpretation of average J couplings may be difficult in temperature regions where these effects dominate the appearance of the spectrum. Qualitative comparison to a similar effect in a 1,25–bis(alkyl) biradical observed at 40%C shows that a different theoretical treatment of the line shapes and SCRP intensities are required for spectral simulation of biradical TREPR spectra at these temperatures. The relationship between the dynamic effects seen in biradical spectra and those observed in micellized RPs will be discussed.

CIDEP/RYDMR/MFE STUDIES ON THE SPIN DYNAMICS OF RADICAL-ION PAIR: TMPD CATION AND SOLVATED ELECTRON

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The photolysis of TMPD (*N,N,N',N'*-tetramethyl-1,4-phenylenediamine) has been investigated by several groups using a time-resolved EPR method. The CIDEP data showed quite interesting but a bit complicated results. It depends upon the experimental conditions such as the light flux. Here, one of important aspects of this system provided by photoconductivity detection will be given. The discussion about the spin dynamics of the radical-ion pair (RIP) including CIDEP will be presented. Furthermore, the development of photoconductivity detected magnetic resonance (PCDMR) will be presented as a new method to investigate radical-ion pair systems.

In the case of moderate photolysis of TMPD by the wavelength of near UV region, mono-photonic ionization takes place through the intermediate RIP formed from the excited singlet state.[1] In the present system, TMPD in 2-propanol/cyclohexanol mixed solvent was ionized by the UV (308 nm) laser light. A specially designed flat quartz-flow cell with platinum electrodes (light path of 0.3 mm) was installed inside of an EPR cavity of TE_{011} mode to observe a transient photoconductivity.

This system showed the magnetic field effect (MFE) on the transient photocurrent.[2] The increase of the magnetic field increased the photocurrent as shown in Figure 1. This is rationalized by the dissolved degeneracy of the triplet spin states by Zeeman effect which makes the S-T mixing inefficient. Therefore, the triplet quenching rout is obstructed and the population of RIP does not decrease so fast. Consequently,

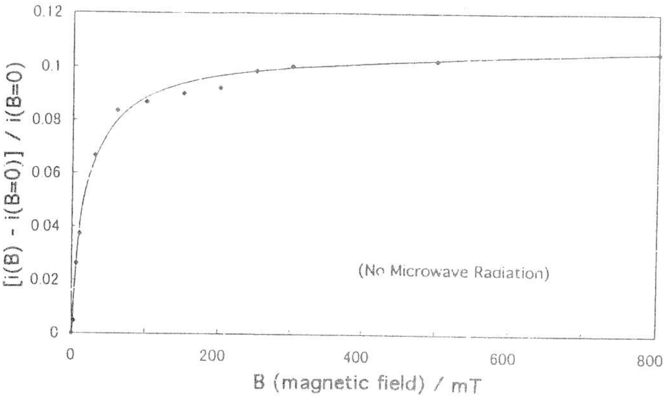

Figure 1. The magnetic field effect upon the photocurrent.

escaping ions from RIP in solvent cage increase. From this data, the contribution of the hyperfine mechanism was confirmed.

Since the electron paramagnetic resonance conditions and application of high microwave power to this system may modulate the reaction pathway of RIP, one can detect the conductivity change as the electron paramagnetic resonance (EPR) spectrum of a transient RIP. Therefore, photoconductivity detected magnetic resonance was tried to develop a new method to investigate the systems of RIP formed in the photochemistry. The trial of photocurrent detection of EPR spectrum of RIP was in success under the microwave power of 10 W as shown in Figure 2. The g-factor of the center position was close to that of the ordinary organic radicals. The spectral shape was extremely broad and the middle region seemed to become almost flat or slightly dipped. The solvated electron was not apparently observed. The decrease of the current at the resonant field is due to the enhanced mixing of all the spin states which accelerates the geminate recombination through the triplet manifold. The flattening of the middle region is due to the slight obstruction of the intersystem crossing by state locking. However, the microwave magnetic field (B_1) was about 0.3 mT in the present conditions which was too weak to induce such a locking. The broadening of the spectral shape is also mysterious. At this stage, most probable explanation of the spectrum may be the observation of the reaction change by the microwave transition of the radical-ion pair state having a J(exchange interaction)-coupling and the J is modified by the dynamic motion of RIP. The relation between the present data and CIDEP will be discussed in the talk.

This technique may become one of the powerful methods to clarify the spin dynamics and structures of transiently formed radical-ion pairs in many photochemical reactions.

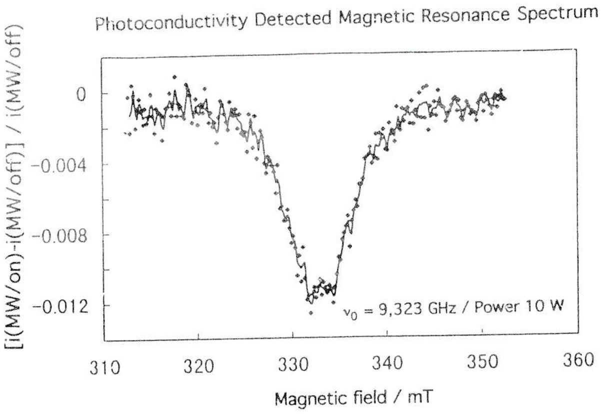

Figure 2. The PCDMR spectrum of the transient RIP which is time integrated between 1.5 and 4.4 μs.

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Time-resolved CIDNP investigation of the kinetics and mechanisms of photoreactions of biradicals and free radicals

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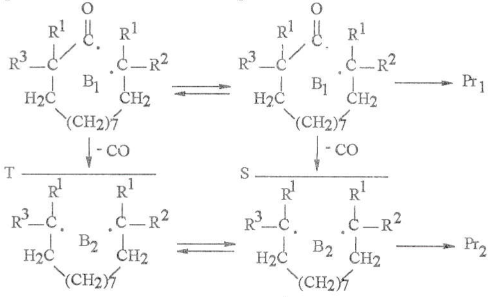
The flash-CIDNP technique based on pulsed laser initiation of photochemical reactions followed by pulsed detection of the NMR spectra of polarized reaction products is a valuable tool for the elucidation of the kinetics and mechanisms of radical reactions in solution. The advantage of this method is the combination of the high spectral resolution of NMR for the identification of the reaction products with the essentially large CIDNP enhancement factors of the polarizrd products, which makes the method very sensitive.

Recently we have increased the sensitivity of the NMR probe by a new home-made 300 MHz resonator and improved the time-resolution of the hardware to 25 ns. This allow us to investigate the kinetics of the geminate evolution of consecutive biradicals during the photolysis of several α-substituted large-ring cyclic aliphatic ketones. At high magnetic fields, the S-T_0 transitions are the main channels of ISC, and the characteristic time of these transitions serves as an internal clock for chemical transformation of consecutive biradicals. The rate of decarbonylation, which depends on substitutients, can be considered fast or slow in comparison with the period of singlet-triplet oscilations in the biradicals. It has been experimentally shown that in these two limits the CIDNP kinetics are essentially different.

In the above ketones, the photoinduced cleavage of α-C-C bonds results in the formation of alkyl-acyl biradicals B_1 in the triplet state. The latter are subject to decarbonylation, which therefore plays the role of the above-mentioned chemical transformation. In this case, the reaction scheme can be presented as follows:



where Pr_1 and Pr_2 denote the sets of products of acyl-alkyl (B_1) and bis-alkyl (B_2) biradicals, respectively.

At high magnetic fields, the signs of the net nuclear polarizations of Pr_1 and Pr_2, as well as the CIDNP kinetics, depend on the rate of decarbonylation. For the alkyl-acyl biradicals arising during the photolysis of trimethyl- (R^1,R^2=CH_3, R^3=H) and tetramethyl- substituted (R^1,R^2,R^3=CH_3) ketones as well as for 2-hydroxy-2,12-dimethylcyclododecanone (R^1=CH_3, R^2=OH, R^3=H), **decarbonylation is slow** compared to the characteristic time of the geminate processes in long-chain biradicals (tens of nanoseconds). In this case, biradical B_2 is formed in the nuclear spin states that have not reacted in primary biradical B_1. Thus, the products Pr_2 of the **secondary biradical carry an escape type polarization**, which is opposite in sign to the geminate one. For Pr_1, the net CIDNP kinetics passes through a maximum and reaches a nonzero stationary value, which is determined partly by the rate of decarbonylation. For Pr_2, the net nuclear polarization increases monotonously in time and reaches a stationary value.

For the "fast" decarbonylation, which is the case with 2,12-dihydroxy-2,12-dimethylcyclododecanone (R^1=CH_3, R^2=R^3=OH), **the CIDNP "memory effect" was observed**. This implies the same nuclear polarization signs of the net CIDNP effects for Pr_1 and Pr_2 at short times. Under our experimental conditions, the CIDNP signals of Pr_1 are constant in time, while the nuclear polarization of Pr_2 decreases and changes its sign at relatively long times.

Model calculations of the geminate recombination kinetics of consequtive biradicals are based on the numerical solution of the stochastic Liouville equation for the Fourier transform of the biradical spin density matrix. A detailed kinetic analysis of the CIDNP effects allows us to reveal all steps of the chemical transformations of the alkyl-acyl and bis-alkyl biradicals, to estimate the probability of the "hidden" back recombination of the biradicals to the initial ketone, as well as to determine the product distribution.

Combination of laser flash-photolysis, steady-state and flash-CIDNP methods allows quantitative investigations of the reactions with not-well established mechanisms. The **photo-Fries rearrangement** was first discovered in 1960. Over the years this phenomenon has been extensively studied and has been observed in various aromatic compounds; however, data on the rate constants of the elementary stages are lacking. This reaction is of obvious academic interest. In addition. it appears to be a significant mode of degradation of polycarbonates, polyesters, polyamides, and other technologically important materials. In this work, we employed the above-mentioned experimental methods for a detailed investigation of the phototransformation of 1- and 2- naphthyl acetates, which are typical photo-Fries rearrangement reactions. It has been shown by laser flash-photolysis that in the irradiated solution of 1-naphthyl acetate (**I**) and 2-naphtyl acetate (**II**) naphtoxyl radicals are formed from the exited singlet state of the corresponding molecules and low-reactive triplet states of the initial compounds. It has been established that the triplet-born radical pairs make the main contribution to the CIDNP of the photo-Fries rearrangement products. The piperylene effect on the genimate CIDNP signal intensities, the transient absorbtion spectra, and the reaction yields sugges that **the process involves two different triplet states of naphtyl acetates (I and II)**. The main channel of the lowest triplet state decay is the triplet-triplet annihilation, while the CIDNP effects of the photo-Fries rèarrangement products result from the decay of the upper triplet states of **I** and **II** with lifetimes of a few nanoseconds. The kinetics of the CIDNP formation in the reaction products was analyzed, and the rearrangement rate constants of the preceding intermediates in the photolysis of **I** at room temperature were estimated.

Steady-state and time-resolved CIDNP and flash photolysis were used in a detailed study of the reversible electron transfer reaction during the photolysis of the $\mathbf{C_{60}}$ and $\mathbf{C_{60}(NO_2)_n}$ fullerene derivatives with triethylamine in solvents of different polarities. The polarization of CH_2 protons of $N(CH_2CH_3)_3$ unambiguously testifies the formation of ion-radical pairs. The kinetics of the formation of ion-radical pairs as well as subsequent degenerate electron exchange between the cation-radicals of triethylamine and diamagnetic molecules of triethylamine in the bulk were analyzed.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (Projects No. 96-03-32930 and No. 96-03-33982) and the Fundation of Intellectual Collaboration (Project No. 96141 "Flash")

ORTHO- AND PARAHYDROGEN INDUCED NUCLEAR SPIN POLARIZATION DURING TRANSITION METAL CATALYZED REACTIONS

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Emission and enhanced absorption lines occur in the NMR spectra recorded during homogeneous hydrogenation reactions, if enriched fractions of the spin isomers of dihydrogen are used namely either parahydrogen or orthohydrogen. As such the spectra resemble those resulting from the **C**hemically **I**nduced **D**ynamic **N**uclear **P**olarization (**CIDNP**) phenomenon, which is caused by free radical intermediates. Here, however, a change of the symmetry due to the hydrogenation causes seemingly similar effects, even though no free radical intermediates occur. The phenomenon has been named **PASADENA** or **PHIP** (**P**ara**H**ydrogen **I**nduced **P**olarization). The associated signal enhancement of PIOT over conventional MMR spectroscopy can reach values of up to 10^5.

An apparatus is described, which provides for a continuous flow of enriched parahydrogen (51 %) at pressures up to 20 bar, and for batches of enriched orthohydrogen (85 %) at ambient pressure. Liquid nitrogen is used as a coolant in either case. Integrated thermal conductivity cells allow a quantitative determination of the corresponding ortho/para ratios of the hydrogen. The enriched ortho- or parahydrogen has been used for *in situ* NMR studies of hydrogenation reactions using specially designed probes which allow investigations of gas/liquid reactions under continuous flow conditions The same apparatus has also been used successfully to enrich ortho- and paradeuteriurn mixtures.

Using this apparatus, it is possible to take advantage of the PASADENA / PHTP phenomenon to introduce nuclear spin polarization into the educts of subsequent reactions. This can be achieved via an initial homogeneous hydrogenation using para- or ortho-hydrogen of a suitable precursor to this educt. If, for example, reactions of alkenes are to tie investigated, a, suitable alkyne may be used to generate the corresponding alkene via a hydrogenation step. i.e., if reactions of ethene are to be studied, homogeneous hydroge-nation of acetylene using parahydrogen allows to generate the ethene with strong nuclear polarization not only of its protons, but also of its ^{13}C nuclei.

The examples investigated include hydrogenations of various alkynes and alkenes using a variety of transition metal calalysts. The subsequent reactions investigated include, for example, brominations.

Reversible reactions can also he investigated conveniently using the parohydrogen labeling method. The associated nuclear spin polarization does not only guarantee strong signal enhancements, but it also highlights the hydrogens, which initially stem from the parahydrogen. This, fact can be used to advantage to study their fate during reversible reactions, as will be outlined using a number of characteristic examples.

SPIN DYNAMICS IN A SEQUENCE OF RADICAL PAIRS

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We have investigated theoretically spectroscopic manifestations of a spin dynamics in a sequence of two radical pairs in time- resolved continuous wave EPR experiments. We found that quantum beats of the second radical pair EPR line intensities demonstrate phase shift which arises from a coherence transfer from the first radical pair. This effect might be used to reveal indirectly the first very short lived radical pair in a sequence..

Control of Radical Pair Lifetime by Microwaves and Magnetic Fields

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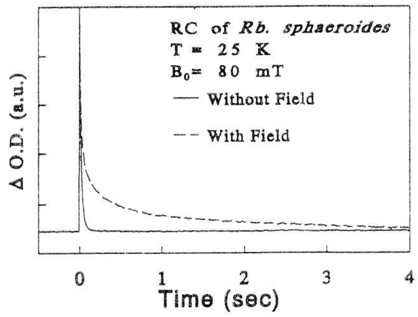

Radicals produced by illumination or ionizing radiation are often produced in pairs, which quickly decay by recombination or by diffusion and subsequent reactions. For maximizing the yield of products, and for facilitating the study of reaction pathways, it is desirable to minimize the probability of radical pair recombination. We present two methods for controlling the radical pair lifetime: One through the application of a pulse of resonant microwaves in the presence of a high magnetic field,[a] and one through the application of a comparatively weak magnetic field immediately *after* the exciting light flash. In the first method, the two $T_\pm$ radical pair triplet states are coherently populated, from which the pair cannot recombine directly to the singlet ground state because of spin conservation. In the second method, the four radical pair levels are initially about equally populated, and the application of the magnetic field separates the (populated) $T_\pm$ levels from the (mixed) S_0 and T_0 levels. For both methods, the lifetime of a considerable fraction of the radical pairs is increased to a value corresponding to the spin-lattice relaxation time. We illustrate the two methods with a photosynthetic photochemical reaction, where we have achieved an increase in radical pair lifetime of up to two orders of magnitude at cryogenic temperatures.

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Multiple quantum pulsed ENDOR spectroscopy by time proportional phase increment detection

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Multiple quantum ENDOR spectra of the PNT radical in solution are reported. All expected multiple quantum spectra up to 6th order could be detected with resolved second order splitting by time proportional phase increment spectroscopy. These spectra are in excellent agreement with the calculation based on the known hyperfine coupling parameters of the sample. Flip angle and off-resonance effects in the detection of multiple quantum spectra have been determined by 2D spectrocopy.

ELECTRON TRANSFER AND SPIN POLARIZATION IN PHOTOSYNTHETIC AND MODEL DONOR-ACCEPTOR COMPLEXES: TIME-RESOLVED X-BAND (9.5 GHZ) AND W-BAND (95 GHZ) EPR EXPERIMENTS

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In primary photosynthesis research the elucidation of the spatial and electronic structures of the donor and acceptor ion radicals involved in the light-induced electron transfer chain is very important. Recent 3 cm (X-band, 9.5 GHz) and 3 mm (W-band, 95 GHz) high-field EPR and ENDOR studies on the primary donor cation radicals $P^{+\bullet}$ (bacteriochlorophyll dimer), the acceptor anion radicals $Q^{-\bullet}$ (quinones), and the charge-separated radical pair ($P^{+\bullet}$-$Q^{-\bullet}$) in photosynthetic bacteria and biomimetic model systems will be presented.

In the case of $P^{+\bullet}$, an asymmetric distribution of the unpaired electron over the dimer halves has been observed. This is of particular interest since it might be relevant for the vectorial electron transfer along only one protein subunit. From single crystals of, for instance, *Rb. sphaeroides* R-26 reaction centers both the hyperfine tensors of various protons and the g-tensor of $P_{865}^{+\bullet}$ have been determined and compared with calculated tensor values. The molecular orbital calculations are based on recent X-ray structure analyses. The results consistently reveal a breaking of the local C_2 symmetry at the primary donor side of the reaction center.

Among the quinone radical anions studied are the electron acceptors of bacterial and plant reaction centers (ubiquinone-10 and plastoquinone-9, respectively). The increased electron Zeeman interaction in high-field EPR leads to almost completely resolved g-tensor components even in disordered samples. They are sensitive probes for specific anisotropic interactions with the environment. Pulsed high-field EPR reveals anisotropic contributions to T_2 relaxation by librational motion of the primary quinone acceptor in its protein binding site.

In the case of the transient correlated coupled radical pair $P^{+\bullet}$-$Q_A^{-\bullet}$ of *Rb. sphaeroides* (Fe replaced by Zn) the spin-polarized high-field EPR spectra allow an unambiguous determination of the relative orientation of the g-tensors of the donor and acceptor parts. Thereby high-precision structure information is obtained on the electron transfer pigments after light-induced charge separation. The results will be discussed with regard to structure- function relationships in primary photosynthesis.

Probing the Spin Dynamics of Radical Pairs by Pulsed EPR

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The spin dynamics of correlated coupled radical pairs results in an out-of-phase echo in pulsed EPR experiments [1]. The intensity of the echo amplitude is modulated as a function of the delay time between the microwave pulses. The modulation frequency is governed by the spin-spin interactions (dipolar and exchange interaction) within the radical pair. Analyis of the modulation frequency spectrum allows the determination of the parameters J and D for the exchange and dipolar interaction, respectively. The r^{-3} distance dependence of D on the separation r of the two spins, therefore, yields information on the geometry of the radical pair. This possibility has been exploited in ref. [2] for the secondary radical pair in the photosynthetic reaction center of *Rhodobacter sphaeroides*. There the distance between the primary donor P_{865} and the quinone acceptor Q_A obtained from pulsed EPR has been compared to the distance known from the crystal structure.

We use the modulation of the out-of-phase echo to compare the geometry of the secondary radical pair in bacterial reaction centers with that in photosystem I. For photosystem I the distance between the primary donor P_{700} and the quinone acceptor A_1 is not yet known from the crystal structure.

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Light-Induced Nuclear Coherences in Photosynthetic Reaction Centers

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Spin-correlated radical pairs are generated as short-lived intermediates in the primary energy conversion steps of natural photosynthesis. In this contribution we report observation of light-induced nuclear coherences in deuterated and ^{15}N-substituted reaction centers of plant photosystem I (PSI) using a high time resolution CW EPR technique (1, 2). Light initiation of nuclear coherence can be understood in terms of the non-adiabatic change of the spin Hamiltonian at the instant of the laser pulse. At time zero the radical pair is formed in a singlet state, which is not an eigenstate of the radical pair Hamiltonian. This implies formation of zero quantum electron coherence between two of the four electron spin states and of combined electron/nuclear coherence involving the various nuclei of the radical pair (3). The light-induced coherence is then transferred to observable transverse electron magnetization by means of the continuous microwave magnetic field.

It should be noted that light initiation of nuclear coherence greatly enhances the detection sensitivity due to optical spin polarization (2, 3). Thorough investigation of this phenomenon, observed in the reaction center of PSI, provides detailed information on the electronic structure of the primary donor P_{700}^{+}. There is clear evidence that two chlorophyll molecules, the special pair, form P_{700}^{+} (3). A deuteron matrix ENDOR line, observed for the secondary acceptor, A_1^{-}, is employed to study water channel formation inside the reaction center protein.

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EPR OF THE SPIN-POLARIZED PRIMARY RADICAL PAIR IN PHOTOSYNTHETIC BACTERIA

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Very recently a new transient g=2 EPR signal has been observed in bacterial photosynthetic reaction centres in which forward electron transfer beyond the primary electron acceptor I is blocked [1]. Within experimental error, the new signal disappears with the same, apparently exponential, kinetics as ^3P (the triplet state of the primary electron donor) appears, leading to its assignment to the primary radical pair P+I-, the precursor of 3P. A preliminary analysis of the spin-polarized EPR spectrum (absorptive at low field and emissive at high field, with peak-to-peak width of ~35 G in *Rb. sphaeroides* and ~70 G in *Rps. viridis*), using the spin-correlated radical pair model [2,3], gave approximate values of the rate constant k_T for the formation of ^3P from P^+I^-, and $J(P^+I^-)$, the exchange interaction between P^+ and I^-.

Here we describe a more detailed analysis of both the kinetics and the spectra. Analytical solution of the stochastic Liouville equation in the high field limit [4] shows that although the kinetics of a single radical pair are in general non-exponential, they become so ~20 ns after formation of the pair. However, averaging over the inhomogeneous distribution of hyperfine couplings in the two radicals leads to multi-exponential behaviour, and to different time constants for the radical pair decay and the triplet formation. Such effects are relatively minor, however, on the time scale of the experimental measurement (100-150 ns), and have so far passed unnoticed. The triplet rise time is found to be dominated by the rate constant k S for recombination of the radical pair to the singlet ground state, and by the spread of hyperfine interactions, and almost independent of J(P+I-) and k . The kinetics of T formation of 3P therefore provide an accurate value for k_S. Comparison of the observed lifetimes for *Rb. sphaeroides* in the absence (~53 ns) and presence (~38 ns) of the reduced acceptor Q- gives estimates of the exchange interaction between I^- and Q^- (4±1 G).

To interpret the spin-polarized EPR spectra of P^+I^-, the spin-correlated radical pair model was extended to include the dependence of the polarization on the rate constants k_S and k_T, differential lifetime broadening of the four allowed EPR transitions, and integration over the inhomogeneous distribution of hyperfine interactions. The simulated spectra are found to be sensitive to k_T, and the sign and magnitude of $J(P^+I^-)$, but indifferent to k_S within reasonable bounds. For small values of k_T , the peak-to-peak separation in the simulated spectra is approximately $4J(P^+I^-)$: larger values of k_T broaden the spectra and push the extrema further apart. Spectral simulations, using $J(P^+I^-) = 5$ G [5], give values of k (~9×10^8 s^{-1}) consistent with low temperature RYDMR measurements [5].

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DETECTION OF SPIN-POLARIZED EPR SIGNALS BELONGING TO THE PRIMARY RADICAL PAIR IN BACTERIAL REACTION CENTERS.

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Introduction. Primary photochemical stage of photosynthesis comprises a chain of electron-transfer reactions, which is triggered by a quantum of light, absorbed by photosynthetic reaction centers (RCs). For bacterial photosynthesis the simplified scheme of the process is:

$$\underset{(0)}{PI(Q_AFe^{2+})} \xrightarrow{h\nu} \underset{(*)}{P^*I(Q_AFe^{2+})} \rightarrow \underset{(1)}{P^+I^-(Q_AFe^{2+})} \rightarrow \underset{(2)}{P^+I(Q_A^-\,Fe^{2+})},$$

where P is the primary electron donor, a bacteriochlorophyll dimer, I is the intermediate electron acceptor, a bacteriopheophytin, and (Q_AFe^{2+}) is the primary acceptor, a magnetically coupled complex of ubi- or menaquinone and non-heme iron. In normally functioning photosynthesis state (1) is formed in ca. 3 ps after RC excitation. In about 200 ps it converts into the state (2). If electron transfer beyond I is blocked, the lifetime of state (2) increases ca. 100-fold, and the originally singlet radical pair P^+I^- (RP1) may populate its triplet state. RYDMR and MARY were applied to the study of this state [1,2] yielding, though sometimes in an indirect way, the values of exchange interaction and recombination rate constant of ^{3}RP1. However, attempts to obtain such information in a more direct way from EPR measurements were so far not successful. Here we report that using adequate time resolution it is possible to detect EPR signals of RP1 in RCs of photosynthetic bacteria.

Materials and Methods. The following RC preparations were studied:

1. *Rhodobacter sphaeroides* R26 with native pigment composition (R26);
2. *Rhodobacter sphaeroides* R26 with both bacteriopheophytin molecules chemically replaced by pheophytin *a* (mR26);
3. *Rhodobacter sphaeroides* R26, quinone-depleted (dQ);
4. *Rhodopseudomonas viridis* (Vir).

A few measurements were carried out on D1-D2-cytb559 complexes of higher plant photosystem II (PSII). In Q_A-containing RCs the primary acceptor was reduced by adding sodium ascorbate and freezing in the light. EPR measurements were performed as in [3]. Laser flashes of 4 ns durations were used for sample excitation, and the signals were collected with a boxcar (100 ns or 20 ns gate). To obtain the highest time resolution, in some experiments Q-factor of the EPR cavity was decreased to ~200.

Results. In the course of flash-EPR studies of the ^{3}P state in mR26 a new feature in the central part of the triplet spectrum was detected (data not shown). The g=2 signal could be observed only with the boxcar gate delays after flash (DAF) of the order of 100 ns. Similar short-lived signals were subsequently detected in all the bacterial preparations studied (see Fig.1 for Vir). No g=2 signals could be seen in PSII. Applying the boxcar gate 20 ns we could measure time evolution of the new g=2 and of ^{3}P signals step-by-step. They demonstrated parallel kinetic behaviour (data not shown). This is a strong indication that the new g=2 signal belongs to the RP1, which is the precursor of ^{3}P

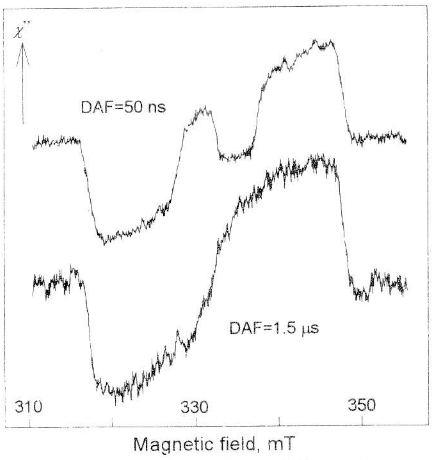

Figure 1. Time evolution of the EPR spectrum of *R.viridis* RCs at 210 K measured with the boxcar gate 100 ns.

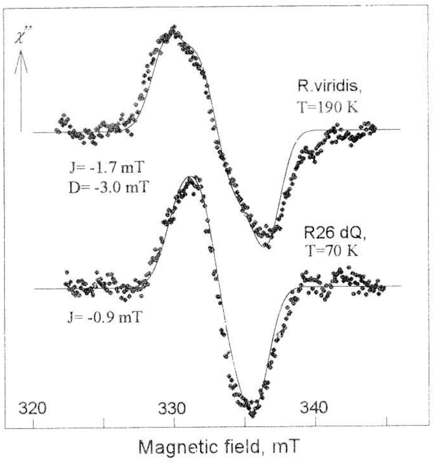

Figure 2. Experimental g=2 signals (dots) after ^{3}P signal subtraction, and their computer simulations (solid lines).

At any value of DAF the g=2 signal overlaps with the signal of ^{3}P. To suppress the latter we took advantage of different temporal properties of the signals. At DAF ≥ 1 μs the detected EPR signal is solely due to the ^{3}P, and could be subtracted from early signals with appropriate scaling. Fig.2 shows the examples of the g=2 signals after such subtraction. These spectra were then simulated within the framework of spin-correlated radical pair formalism [4]. While fitting, increased ΔBpp of separate P^+ and I^- radicals had to be implemented, related to a short lifetime of RP1. Lifetimes of triplet RP1 could be estimated from the procedure, giving ~3 ns for R26 and dQ, and ~6 ns for Vir RCs. The value for R26 is close to that reported earlier [2]. Triplet RP1 lifetimes are much shorter than that determined from time-resolved optical measurements. It means that the triplet recombination rate is faster than the rate of S-T conversion in RP1, so that optical lifetime is mostly determined by the latter. Thus, long optical lifetimes of RP1 do not necessarily result in favourable conditions for RP1 EPR detection. Slow population of the triplet RP1 and its fast recombination would lead to low signal amplitudes, which probably is the case for PSII. Adversely, mR26 demonstrate a short optical lifetime of RP1. This explains the discovery of the RP1 EPR with these preparations.

The effects of distribution of the RP1 parameters will be discussed.

Financial support from NWO and INTAS is gratefully acknowledged.

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ELECTRON SPIN ECHO OF SPIN-POLARISED RADICAL PAIRS IN PHOTOSYNTHETIC REACTION CENTERS

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Radical pairs were studied by electron spin echo (ESE) spectroscopy in photosynthetic reaction centers (RCs):
(i) Zn-substituted bacterial RCs of purple bacterium *Rhodobacter sphaeroides* R26.
(ii) plant photosystem I and quinone-reconstituted plant photosystem I.
(iii) Zn-substituted, Mn-depleted plant photosystem II.
The primary light-induced reactions in all these systems result in formation of transient spin-polarised radical pairs P^+Q^- where P denotes the primary donor (chlorophyll or bacteriochlorofyll dimer) and Q denotes primary acceptor quinone.

The experimental setup comprised of Bruker ESP 380 FT EPR spectrometer and Continuum Surelite laser pumping optical parametric oscillator (OPO). Full excitation of the EPR line was employed.

All systems were found to produce a remarkable light-induced ESE signal. This signal is out-of-phase and strongly modulated, in agreement with recently developed theory [1]. Modulation is induced by dipolar and exchange spin-spin couplings in the pair. Fourier transformation of the modulation decay allows values of these couplings to be determined with high accuracy [2].

When the echo-forming microwave pulses were applied not later then 40 ns after the laser flash, a transient behavior of the echo shape was observed [3]. This was ascribed to quantum beats between sublevels of the pair. An additional echo signal was also observed when the time delay between the laser flash and the first microwave pulse was strictly the same as that between the first and the second microwave pulses. This echo was ascribed to double-quantum coherence.

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THE CIDEP SPECTRUM THEORY OF GEMINATE RADICAL PAIRS

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The CIDEP effect is formed under the action of magnetic interaction (hfi, Zeeman, exchange, dipole-dipole interactions) in radical pairs generated by chemical reactions. The existing theories of the phenomenon under discussion usually assume the formation of the effect and its detection are separated in time. In this case, the mw-field power absorbed by the spin system is directly proportional to its magnetism, and the absorption line is of Lorentzian form. Nevertheless, it is clear that this is by no means always the case [1]. For example, if sufficiently powerful, the mw-field not only serves to detect the ESR spectrum, but it can also produce noticeable effect on spin dynamics of radical pairs, and, therefore, on the formation of the CIDEP effect even in not very viscous solutions. Of course, this influence will take place only in the case where the mw- -field is switched on at the moment of the pair generation, rather than after the escape of radicals from the cage.

The present contribution reports the CIDEP theory with allowance for the mw-field influence. An important element of the theory is the procedure of decoupling of the corresponding average values over the reaction and exchange interaction zones. These average values arise from the averaging of the basic kinetic equation for the density matrix of radical pairs expressed in terms of the Green's functions. The calculation of the Green's function is done by the method of sequential approximations [2,3].

The CIDEP spectrum of free RPs is most easy to calculate. For example, the energy density absorbed (radiated) by the system can be represented as

$$E(\omega) = n\hbar\omega \sum_{\{m\}} \sum_{k=1,2} \frac{\omega_{1k} T_{2k} \left(S_{ky} - \omega_{1k} T_{1k} S_{kz} + (\omega_{km} - \omega) T_{2k} S_{2x} \right)}{1 + \omega_{1k}^2 T_{1k} T_{2k} + (\omega_{km} - \omega)^2 T_{2k}^2} \tag{1}$$

where $\omega_{km} = \omega_{0k} + \sum_i a_{ki} mi$ is the Larmour precession frequency of the electron spin of the i-th radical with the given configuration $\{m_k\}$ of nuclear spins, T_{1k} and T_{2k} are longitudinal and transverse relaxation times

$$\vec{S}_k = \mathrm{Tr}\left(\hat{S}_k \sigma \right) \tag{2}$$

The matrix σ is defined by the relative motion kinematics and overall spin dynamics, and is calculated by the method of sequential approximations. The simplest results are obtained at low efficiencies of singlet-triplet transitions.

We believe that a significant advantage of the method is its ability to separate the coordinate-independent spin evolution from reactivity (not necessarily isotropic). The latter can be described both within the framework of analytically solvable models, and on the basis of numerical calculations including those for coupled radical pairs (biradicals, micellar radical pairs, photosynthesis reaction centers, RP in molecular clusters in the gas phase).

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Magnetic Support of Combustion in Diffusion Flames under Microgravity

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1. INTRODUCTION

"Magnetoaerodynamics" is a new research area to control air flows and combustion by using the magnetic force which acts on paramagnetic oxygen gas (1). For example, the magnetically induced air flows were found to promote combustion in diffusion flames when fuel gas flowed toward a weaker magnetic field (2). The magnetic acceleration and deceleration of O_2 and N_2 gas flow were also found to depend on the sign of the magnetic field gradient (1). These phenomena can be explained by the following magnetic attractive force acting on O_2 containing gas:

$$F=(1/2)\mathrm{grad}(\chi \cdot H^2)=(1/2)\mathrm{grad}(P_{O2} \cdot \chi_{O2} \cdot H^2) \qquad \text{Eq.1}$$

H is the magnetic field strength. P_{O2} is the partial pressure of O_2. χ_2 is the volumetric susceptibility of O_2. Since χ_2 is much larger than that of such a diamagnetic gas as N_2, χ is mainly determined by P_{O2}.

We report here the application of "magnetoaerodynamics" to space science. Whenever flames are used for heating specific objects under normal gravity and O_2-containing atmosphere, we rely on natural or forced convection to replenish reactants and direct hot products. Because buoyancy-induced convection is absent in microgravity, diffusion flames were found to become spherical, have low power and eventually be extinguished (3). In order to support combustion in diffusion flames in microgravity, we report here the magnetic control of air flows.

2. EXPERIMENT AND RESULTS

Microgravity environments (about 10 sec, $<10^{-4}$G) were obtained in a 490 m free drop shaft at JAMIC. The experimental setup is illustrated in Fig.1. Magnetic field gradients were obtained by permanent magnets. The magnetic strength (H) shows the maximum value three dimensionally around the origin of the site coordinate. Butane (36 mL/min) flowed along the y-axis in the direction of the decreasing strength of the field. In this situation, air is magnetically supplied to the flame front along the steepest gradient of the fields, as indicated by the solid arrows. Magnetic convection of air is also considered to occur along the y-axis (indicated by the dotted arrow) because of the following relation:

$$\chi = P_{O2} \cdot \chi_{O2} \cdot T_{RT}/T^2 \qquad \text{Eq.2}$$

The other experimental procedures were described in the reference (4). The flame was set both in air and an $50\%O_2/50\%N_2$ atmosphere (Fig.2). As a reference, we tested the diffusion flame without magnets (Fig.2 A-C). As the time of microgravity passed, the flame which showed the typical tear-drop type in normal gravity became spherical and the luminosity significantly decreased similarly to

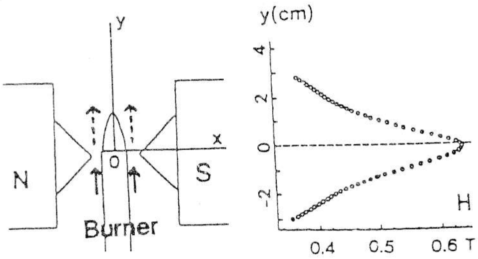

Fig.1 Experimental Setup

the previous studies (3). Specially in air, the flame became invisible after a few sec after the drop and finally extinguished. These facts indicate the difficulty of continuing combustion in microgravity.

On the other hand, when permanent magnets were installed, the flame in normal gravity (Fig.2-A') became shorter and more brilliant than without magnets (Fig.2-A). This magnetic promotion of combustion can be explained by the increase of air supply due to both the magnetic convective and attractive flows similarly to the previous study (2). When the combustion field was changed into microgravity (Fig.2-B',C'), the flame became more brilliant, shorter and wider than in normal gravity. Since there was no gravity-induced convection, the flame became shorter and located inside the highest region of $H(\partial H/\partial y)$. Therefore, gradient magnetic fields affected more efficiently combustion than in normal gravity. Furthermore, it is characteristic that the high luminosity and shape did not change during the duration of microgravity (10 sec), while the luminosity significantly decreased without magnets. Similar result was also observed in air, though the flame was extinguished within 10 sec microgravity duration.

3. DISCUSSION AND CONCLUSION

These experimental results proved that magnetically induced air flows completely supported combustion in microgravity. The vertically long shape of a flame (Fig.2-B,B') indicates the existence of magnetically induced air flow upward. Magnetic convection occurred upward along a dotted arrow above the burner head because combustion accompanies the decrease of magnetic susceptibility (see Eq.2). Below the burner head, air was attracted upward along the solid arrow. The combination of these two kinds of magnetically induced flows is considered to makea vertically flow. The velocity of the magnetically attracted air around the flame front is also calculated by the energy conservation equation:

$$(1/2)\chi \cdot H^2=(1/2)\rho \cdot v^2 \qquad \text{Eq.3}$$

ρ is the density of O_2-containing gas. When $H=0.6T$ and $P_{O_2}=0.5$, the velocity is calculated to be about 46cm/sec.

The present study suggests the potential ability of magnetic fields to control air flows (magnetoaerodynamics).

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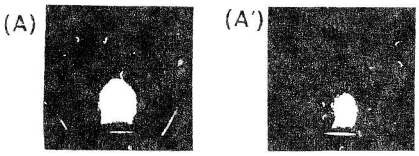
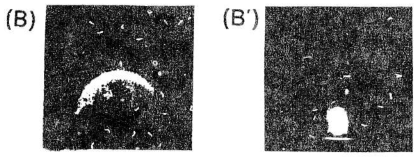
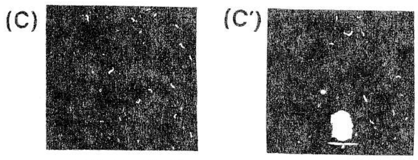


1 G



< 10^{-4}G, 0.76 sec after the drop



< 10^{-4}G, 7.43 sec after the drop

Fig.2 Comparison Between Without (A-C) and With Magnets (A'-C')(50%O_2/50%N_2

Magnetic Depolarization of Fluorescence in Large Molecules

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Magnetic depolarization of atomic resonance fluorescence is well known as the Hanle effect. The Hanle effect of the molecular resonance fluorescence is also known to be feasible in di- or triatomic molecules, and a single rotational level has been assumed to be optically excited in both the theoretical and the experimental treatments presented so far. In medium sized or large molecules where intramolecular dynamics plays a significant role, however, the problem still remains unsettled, how external magnetic fields affect the polarization of fluorescence.

In the intermediate case molecules such as pyrazine or pyrimidine, fluorescence emitted from optically prepared levels is polarized, depending both on the excited rovibrational level and on the vibronic fluorescence band monitored. The excited states of these molecules are mixed states composed of a zero-order singlet state and a number of zero-order triplet states, and the fluorescence resulting from the coherent excitation of these mixed states shows a biexponential decay composed of fast and slowly decaying portions. The polarization spectra of fluorescence of these molecules at zero field across the rotational contour are well simulated for both fast and slow components by assuming resonance fluorescence. This raises a question how the polarization of each of fast and slow components of fluorescence is affected by an external magnetic field in these molecules having strong singlet-triplet interaction; is there any difference between the fast and slow components in magnetic field dependence of polarization except for the difference resulting from the difference of the fluorescence lifetime?

We have examined the field dependence of fluorescence polarization of these azaaromatic molecules in a bulk gas at room temperature or in a supersonic jet with a traditional orthogonal geometry. The intensities of the fluorescence polarized parallel (X) and perpendicularly (Y) to the polarization direction (X) of the exciting light are denoted by $I_{\parallel}$ and $I_{\perp}$, respectively. The degree of polarization (*P*) is defined as $P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$. External magnetic fields, *H*, were applied along the Z axis, which is the propagation direction of the detected fluorescence. By combining the total fluorescence intensity measurement with the decay measurement, the *P* value for each of fast and slow components of fluorescence was obtained as a function of field strength and as a function of time.

Figures show the results of pyrimidine vapor at 0.12 Torr on excitation at the Q-peak of the 0--0 band belonging to the $S_0 \rightarrow S_1$ transition. The *P* value decreases so efficiently from 0.25 to 0.12, as *H* increases from 0 to 50 mT. At *H* above 0.1 T, however, the efficiency of magnetic depolarization becomes much lower and the *P* value is regarded as nearly constant at high fields. The lifetime of the slow component is 90 ns at 0.12 Torr, while the lifetime of the fast one is 2.7 ns. With increasing *H*, the intensity of the slow component relative to the fast one becomes lower since only the slow component is quenched by *H*. At zero field, both decays of $I_{\parallel}$ and $I_{\perp}$ are identical with each other, and the fast and slow components are polarized in the same way. With increasing *H*, both decays become different from each other, indicating that the *P* value of the fast component is different from the slow one. Actually, the slow component is nearly depolarized at 50 mT, whereas the fast component is not depolarized by *H*.

The theoretical treatment of the molecular Hanle effect shows that the *P* value of resonance fluorescence as a function of H gives a Lorentzian shape:

$$P = P_0/\{1 + (2g\mu\tau H/\hbar)^2\},$$

where P_0 is the value at zero field, which depends on the rotational quantum number. $\hbar$, g and μ are Planck's constant divided by 2π, the Lande g factor and the Bohr magneton, respectively, and τ is the lifetime due to the destruction of coherence in the excited state. As the vapor pressure increases, fluorescence lifetime of the slow component becomes shorter and the magnetic depolarization becomes less efficient, suggesting that the above equation is applicable to the slow component. By assuming that τ is the same as the lifetime of the slow component, the g value is evaluated to be 1×10^{-2} on the Q-peak excitation from the magnetic depolarization of the slow component by using the above equation. This g value is regarded as the average over all the singlet-triplet mixed states coherently excited. If above equation is also applicable to the fast component, the field strength where the P value of the fast fluorescence becomes one-half of the initial value is estimated to be 0.2 T by using the above g value and the τ value of 2.7 ns. However, the fast component is not affected by H, even when H is raised up to 10 T. Similar results have been obtained in pyrazine vapor. Thus, the fast component of fluorescence which corresponds to the dephasing decay is not depolarized by H, even when the optically excited singlet state strongly interacts with the triplet state. On the other hand, the slow component of fluorescence in intermediate case molecules is efficiently depolarized by an external magnetic field.

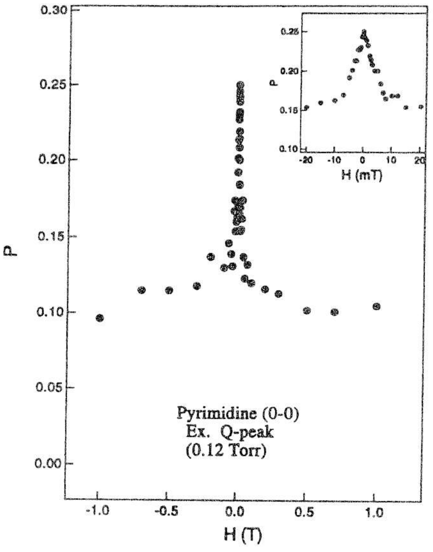

Fig. 1. The degree of polarization (P) of the total fluorescence of pyrimidine vapor as a function of H.

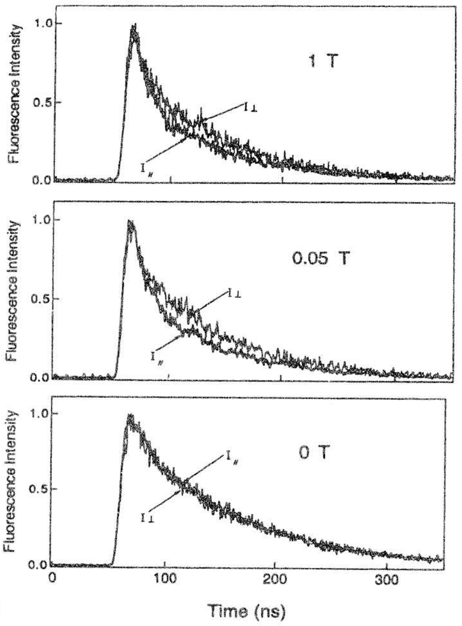

Fig. 2. Fluorescence decays of $I_\parallel$ and $I_\perp$ of pyrimidine vapor at zero field, 50 mT and 1 T (from bottom to top). The maximum intensity is normalized to unity in every decay.

PHOTOCHEMICAL PROCESS OF VAPORIZED CARBON DISULFIDE IN EXTERNAL MAGNETIC FIELD

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1. Introduction

It is known that a magnetic field quenches the fluorescence from a no spin degenerate, singlet excited state of vaporized CS_2.1) The phenomenon is of interest, since the magnetic field can affect the photochemical process in the excited singlet state; we can more easily expect the magnetic field effect on the photochemical processes in spin degenerate states, since the field can shift the energy levels of these spin degenerate states. In fact, it is known that the magnetic field quenches the emissions from the $^2B_2$ state in $NO_2$2) and the $^3\Pi_{0u}{}^+$ state in I_2.3) The magnetic quenching of fluorescence from vaporized CS_2 is due to a direct mechanism and an indirect mechanism.4,5) The direct mechanism is attributed to the direct coupling between the primary state and the secondary state, and the indirect mechanism occurs in an "intermediate case". Imamura et al.6) confirmed that the magnetic quenching of fluorescence of CS_2 is represented as an "intermediate case". In this case, the fluorescence intensity ratio of the slow component to the fast component decreases in a magnetic field.

In the present paper, we study the excitation wavelength dependence of the magnetic field effect on the fluorescence from vaporized CS_2 in a wavelength range of 298-333 nm. The results will be significant to study the interaction between the radiationless transition and the magnetic field effect on the fluorescence. Furthermore, we study the magnetic field effect on the laser-induced aerosol formation from vaporized CS_2. This will be of great interest, since it is an application of the magnetic field effect to chemical reactions.

2. Magnetic Field Effect on Fluorescence as a Function of Excitation Wavelength

Figure 1 shows the decay curves of the fluorescence from vaporized CS_2 excited at wavelengths of 312.679 and 302.414 nm. For the excitation at a wavelength of 312.679 nm, the magnetic field quenches the fast component of the fluorescence, but the magnetic field effect on the slow component is negligibly small. The nano-second time-resolved spectra indicate that the fast component is assigned to the sharp band spectrum and the slow component is done to the broad band spectrum.7) Besides these spectra, Imamura et al.6) found the pico-second component that cannot be observed with the present nano-second time-resolution.

The nonradiative transition of CS_2 is represented by the intermediate case.6) In this case, the fluorescence approximately exponentially decays with fast and slow components; the pico-second component observed by Imamura et al.6) is assigned to the fast component of the intermediate case, and the fast component observed in the present study, as shown in Fig.1, is assigned to the slow component of the intermediate case. The ratio of the pre-exponential factor of the fast component to that of the slow component, i.e., C_f/C_s is approximately proportional to N_{eff} that is the number of the secondary-state levels coupling with the primary state. A magnetic field increases N_{eff}, and hence it increases C_f/C_s. Thus the slow component of the fluorescence is quenched by a magnetic field.

The magnetic field effect is great for the excitation at a wavelength of 312.679 nm, as shown in Fig. 1(a), but negligibly small for the excitation at a wavelength of 302.414 nm, as shown in Fig. 1(b); the magnetic field effect is very sensitive to the excitation wavelength.

Figure 2 shows the excitation-wavelength dependence on the magnetic field effect on the fluorescence in a wavelength range of 298-333 nm. The 1V-43V bands of the V-

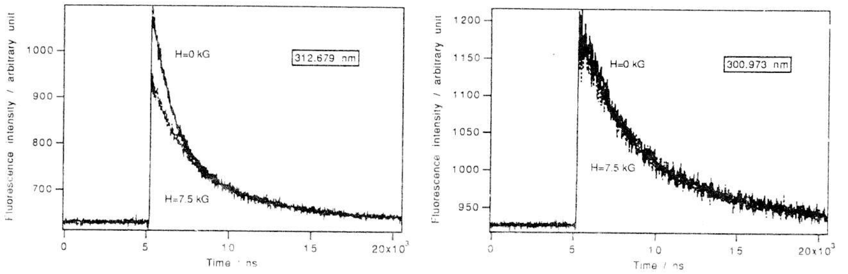

Fig.1 Decay curves of fluorescence from vaporized CS_2 in a magnetic field of 0 and 7.5 kG. Excitation wavelength: (a) 312.679 nm, (b) 302.414 nm.

system assigned to the $^1B_2$-$^1\Sigma_g^+$ transition[8] are included in this wavelength range. In this figure, the ratio of the fluorescence intensities at t=0 at a magnetic field of 0 and 7.5 kG is plotted as a function of excitation wavelength. This figure indicates that the magnetic field effect is very sensitive to the excitation wavelength. Furthermore, it is found that the magnetic field effect increases with wavelength, on the whole. Since the level density of the secondary state, i.e. N_{eff}, increases with excitation energy, C_f/C_s increases with an increase in excitation energy. The decrease in the magnetic field effect with a decrease in excitation wavelength is due to the increase in the level density of the secondary state, i.e., N_{eff}, or the increase in C_f/C_s. Hence, the magnetic field effect is less, when the interaction between the primary state and the secondary state is greater at zero magnetic field.

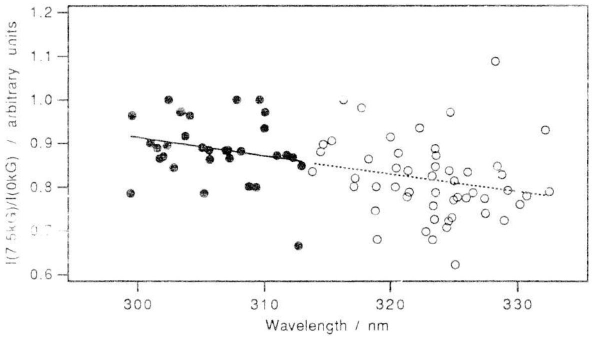

Fig.2 The wavelength dependence of the magnetic field effect on fluorescence of vaporized CS_2.

3.Magnetic Field Effect on the Laser-Induced Aerosol Formation

We study the magnetic field effect on the laser-induced aerosol formation from vaporized CS_2, and discuss it by comparing with the magnetic field effect on fluorescence.

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SPIN-LATTICE RELAXATION MECHANISMS IN AMORPHOUS AND POLYCRYSTALLINE RUBRENE FILMS REVEALED BY MAGNETIC FIELD EFFECTS ON LUMINESCENCE

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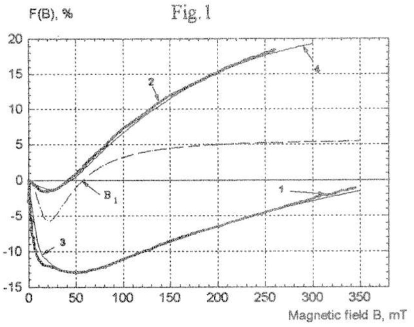
Amorphous and polycrystalline rubrene films were chosen as a model system for studies of magnetic field effects (MFEs) controlling generation and recombination of pairs of triplet excitons. Thin films of rubrene were deposited in vacuum onto polished quartz surfaces and subjected to different temperature regimes. Rubrene films deposited on surfaces at room temperature possessed no crystalline structure, while those deposited on cold surfaces (170 K) and then promptly heated to room temperature, showed crystallization lasting several days. Microcrystals of rubrene were seen by microscope.

Photoluminescence of rubrene films in constant magnetic field was studied. The characteristic curves of relative luminescence change in a magnetic field (henceforth denoted as the MFE) are presented in fig. 1. The shape of MFE curves is similar to that proposed by Johnson-Merrifield approach (JMA) which describes the magnetic field controlled generation of pairs of triplet excitons (fission) [1]:

$$S_1 \underset{K_2}{\overset{K_1}{\rightleftarrows}} [T_1 \ldots T_1] \xrightarrow{K_{-1}} T_1 + T_1$$

However, some new features were found: 1) Both for amorphous and crystalline films MFE functions *F(B)* (dotted curves 1 and 2, respectively, in fig.1) differ from those predicted by the JMA . In particular, the experimental curves do not saturate in the field up to 350 mT, although the zero splitting parameter D is relatively small (57 mT). 2) Sharp decrease of the luminescence intensity for the crystalline films was observed at B<20 mT. No such a decrease was observed for amorphous samples (fig.1, dotted curve 2). 3) In the crystalline films the field B_1, where $F(B_1)=0$, is much larger than that in amorphous films ($\sim D = 57$ mT). 4) Strong non-linear dependence of MFE on the intensity of excitation light is observed in crystalline films. On the other hand, the MFE in amorphous films does not exhibit such a non-linear dependence.

Fig.1



The dependence of MFE curve shape on the intensity of excitation light is well explained in terms of JMA regarding that in microcrystals the steady state concentration of triplet excitons is high, so the process of their fusion becomes significant. Fusion of triplet excitons is a second order process in their concentration and leads to the opposite (in comparison with fission) MFE sign. Superposition of fusion and fission gives rise to seeming decrease of MFE magnitude with increase of excitation light intensity.

Other unusual features of MFEs in rubrene crystals could hardly be explained by any of approaches, such as hyperfine interaction, Δg-mechanism, magnetic dipole interaction of triplet excitons. Analysis showed that only spin-lattice relaxation (SLR) is able to describe both qualitatively and quantitatively the MFE in rubrene films.

Numerical solution of stochastic Liouville equation (SLE) was carried out. In the case of amorphous film the major SLR mechanism was supposed to be hopping of triplet excitons over chaotically oriented molecules. For model calculations, the finite number of randomly oriented molecules was taken, and SLE was solved for triplet exciton density matrix distributed over those molecules. In the case of polycrystalline film the SLR was due to thermal librations of molecules and was described by the relaxation superoperator within the short correlation time approximation [2].

The calculation results are shown at figs. 2,3 for amorphous and polycrystalline films, respectively. In fig. 2 the family of MFE curves is compared with the experimental curve. Calculations have been made for different values of K_{-1} and K_2. For $K_{-1} = 2*10^8$ s^{-1} and $K_2 = 10^9$ s^{-1} we have obtained the hopping rate $K_h \approx 7*10^9$ s^{-1} which corresponds to the value of the diffusion coefficient of T-excitons $\approx 10^{-5}$ cm^{2}s^{-1} quite common for molecular crystals (see [1]).

The MFE dependencies *F(B)* calculated for polycrystalline film for different values of K_{-1} and K_2 are displayed in Fig. 3 together with the experimental results. It is seen that the calculated function *F(B)* reproduces quite well the experimental MFE dependence and, in particular, the sharp rise of the MFE amplitude at low fields. Especially good agreement is observed for the parameters $K_{-1}=10^7$ s^{-1} and $K_2 = 2*10^7$ s^{-1} which are of the order of those reported in [3-5].

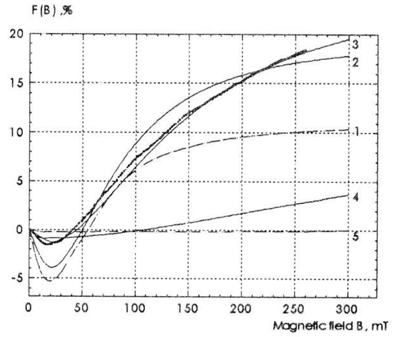


Fig.2

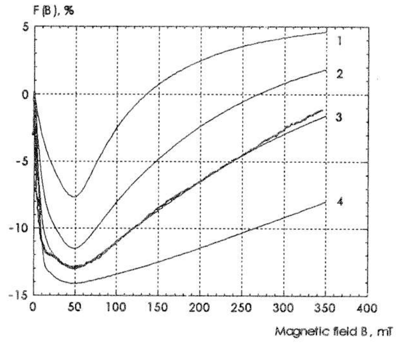


Fig.3

Acknowledgements

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Magnetic quenching of the gaseous fluorescence by the direct and indirect mechanisms.

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Magnetic quenching of the molecular emission in the gas phase provides us unique information about energy transfer processes concerning excited states. In particular, the effect of fluorescence of NO_2 was discovered by Solarz, Batler and Levy in 1973 as the first example of the effect due to on excited states of polyatomic molecules. In this case, the magnetic quenching has been observed for the doublet excited states. In 1974 Matsuzaki and Nagakura have discovered the magnetic quenching of a non-magnetic singlet excited state of CS_2. These works opened à new research field for investigation dynamic behavior of excited states in the gas phase. Since then, external magnetic field effects on gaseous fluorescence have been found for a number of molecules such as SO_2, carbonyls, diazines and triazine.

The observed effects have been explained by the direct and indirect mechanisms (DM and IM). In a frames of DM, levels {|*s*>} of the fluorescent state and levels {|*q*>} of the neighboring "dark" states, while in case of IM, these levels are coupled by a magnetic field in the second, third and other orders of the perturbation theory.

In the present study, we have investigated the magnetic field effects of the NO_2, SO_2 (short-living component) and $(COF)_2$ ($0^0{}_0$-band fluorescence of the $A^1A_u \rightarrow X^1A_g$ transition) fluorescence under the time resolved experiments.

NO_2 and SO_2.

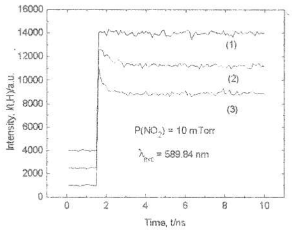

Figure 1a

It was found that in the presence of a magnetic field, the fast component induced by a magnetic field appears in the NO_2 and SO_2. Lifetime and amplitude of this component are dependent of a magnetic field (*B*). Typical dependences of the NO_2 and SO_2 fluorescence decay are shown in Figures 1a and 1 b. The observed data were explained by DM, in a frames of which, we assume

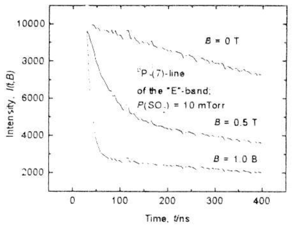

Figure 1b.

that the $<^2B_2|\boldsymbol{H_z}|^2A_1>$ (= V_B) and $<^2B_1|\boldsymbol{H_z}|^2A_1>$ (=V_B) coupling are significant for NO_2, and $\{\alpha<^1A_2|\boldsymbol{H_z}|^1A_1>+\beta<^1B_1|\boldsymbol{H_z}|^1A_1>\}$ (= V_B = b) coupling is significant for SO_2. Here, $\boldsymbol{H_z}$ is the Zeeman operator. Using these statements, we have estimated the V_B/B and effective level density ($\rho_q(E)$) values for the presented cases: $\rho_q(E)$ and "b" are ca.126/cm^{-1}, 285/cm^{-1} and 1.2•10^{-2}cm^{-1}T^{-1}, 0.8•10^{-2} cm^{-1}T^{-1} at λ_{exc} = 496.11 nm and λ_{exc} = 589.84 nm, and $\rho_q(E)$ = 8.5•10^3/cm^{-1} ($\rho_{vib} \approx$ 10^3/cm^{-1}) and b = 2.4•10^{-4} cm^{-1}T^{-1}. respectively for NO_2 and SO_2. The anomalous valuse of $\rho_q(E)$ was explained by the magnetic field-induced coupling of the different nuclear-spin-rotational components in the NO_2 case and by the spin-orbit coupling of the low-lying triplet levels and ground state levels in the SO_2 case.

(COF)$_2$.

It was found that the fast component of the $0^0{}_0$-band fluorescence decay of the $A^1A_u \rightarrow X^1A_g$ transition appears in the presence of a magnetic field. Lifetime of this component is not dependent of B, while it amplitude increases with increasing of B. Typical decay of this fluorescence is shown in Figure 2. Lifetime of the slow component increases in the presence of a magnetic field at $P((COF)_2)$ = 0.3 mTorr. Obtained data were explained by IM. Magnetic quenching of the $(COF)_2$ fluorescence by IM was also checked by the microwave field effect of the $(COF)_2$ fluorescence. We have observed an additional quenching of the $(COF)_2$ fluorescence in the presence of a microwave field (λ_{MW} = 3 cm). Dependence of the observed effect on the microwave field power is shown in Figure 3. From this Figure, it follows that microwave field effect has a resonance character. We assume that this effect belongs to ODEPR signal of the a^3A_u state.

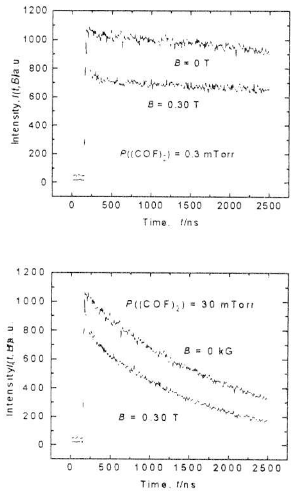

Figure 2.

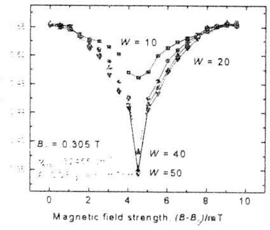

Figure 3.

Magnetoplastic Effect and Spin-Lattice Relaxation in Nonmagnetic Crystals

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The new physical phenomenon - magnetoplastic effect - was found out and investigated in the series of nonmagnetic crystals (NaCl, CsI, LiF, Zn and Al). The phenomenon manifests itself in dislocation displacements as a result of specimen exposing to a static magnetic field in the absence of mechanical loading [1-7].

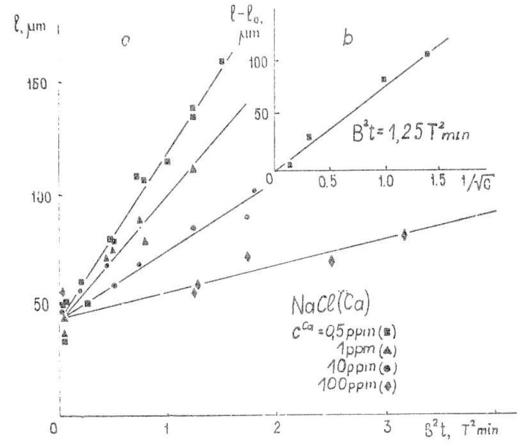

Fig.1

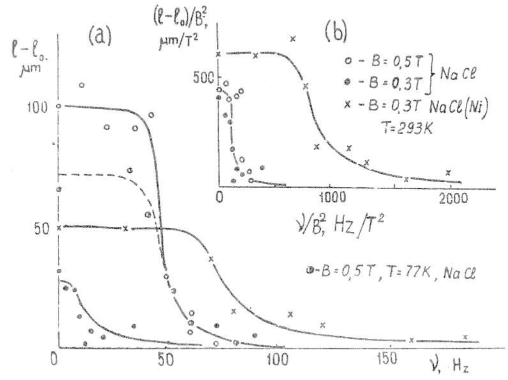

Fig.2

The basic features of the phenomenon are as follows. The average displacement of dislocations ℓ in magnetic field is proportional to the magnetic "treatment" time t_m of the sample and to the squared magnetic induction ($\ell \propto B^2t_m$, see Fig.1a). Dislocations which are oriented parallel to the magnetic field are insensitive to the latter quantity. The dislocation displacement ℓ decreases with increasing concentration C of paramagnetic impurities ($\ell \propto 1/\sqrt{C}$, Fig.1b). The effect is "killed" if diamagnetic impurities are predominant in the crystal. The temperature dependence of the dislocation displacement is very weak: ℓ is virtually identical at 4.2 K and 77 K, and as the temperature increases to the room temperature, the displacement increases by only 15-20%. The density of mobile dislocations increases with the magnetic induction B and increasing time t_m, and it can reach 100% of the density of freshly introduced dislocations. For high values of B^2t_m the displacement ℓ also saturates - at a level corresponding to the average distance between the "forest" dislocations. Rotation of the sample in a magnetic field gives rise to a critical frequency ν_c ($\nu_c \propto B^2$), above which the displacement ℓ drops sharply to zero (Fig2). This value proves to be independent of T and C, but sensitive to a type of impurity, to X-ray irradiation and different for edge and screw dislocations.

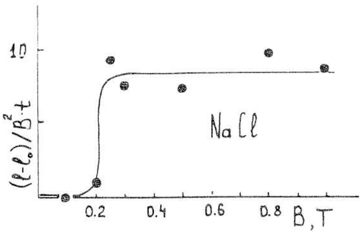

Fig.3

The physical model describing the phenomenon is based on the idea of detachment of dislocations from paramagnetic impurity centers as a result of spin-dependent electronic transitions which are stimulated in the system impurity + dislocation by a magnetic field whose role reduces to removing the spin forbiddenness on the processes which breakdown local barriers. The subsequent motion of the dislocations occursin the field of the long-range internal stresses from other dislocations and, naturally, stops when the displacements reach value of the order of the average distance between dislocations.

A necessary condition for the existence of such effects is that the spin-dependent transition time must be small compared with the spin-lattice relaxation time τ_{sl} of the experimental system. In our case the spin-dependent transition time is practically coincide with the mean time of dislocation depinning from paramagnetic center τ_{dp}, which can be estimated as $\tau_{dp}=k\nu_c^{-1}$ with coefficient $k\sim10^{-2}$.

Knowing, that τ_{dp} grows as $1/B^2$ at decreasing magnetic induction B and that there should be no effect at $\tau_{dp}>\tau_{sl}$, we can also estimate the time of spin-lattice relaxation in our system as $\tau_{sl}\approx\tau_{dp}(B_c)$, where B_c is a critical level of the magnetic field below which there is no magneto-depinnig (Fig.3). This procedure gives for the spin-lattice relaxation time τ_{sl} for the system dislocation+Ca-impurity complex in NaCl crystal at the room temperature the estimate $\tau_{sl}\approx10^{-3}$ s. It is shown also that with decreasing temperature the value τ_{sl} fast grows.

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POSTERS

POSTER 1

Peculiarities of low magnetic field CIDNP and SNP for radical pairs with large HFI constants in homogeneous solutions.

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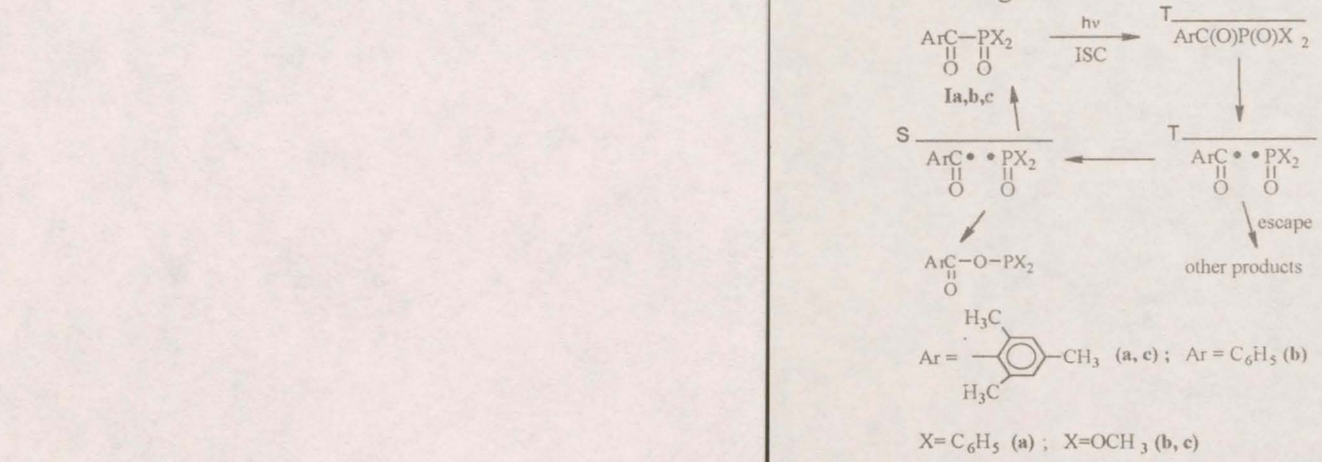
Experimental studies of CIDNP and SNP effects in systems with large HFI constants were carried out with (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (Ia), benzoylphosphonic acid dimethyl ester (Ib), and 2,4,6-trimethylbenzoylphosphonic acid dimethyl ester (Ic). As is known [1], in the photolysis of Ia, C-P bond cleavage from a triplet molecule is observed which results in the formation of trimethylbenzoyl - diphenylphosphonyl radical pair with a single HFI constant (36.5 mT) at the ^{31}P nuclei. In the case of Ib,c, it may be expected that the reaction occurs particularly through the α-cleavage from the triplet state [1] to yield RPs with a single HFI constant of 70.0mT (Scheme 1).

The low magnetic field dependences of ^{31}P-CIDNP obtained in the photolysis of Ia (in ether ■, benzene □, 1,4-dioxane ∇, see Fig.1a) and Ib,c (Ib in acetonitrile o, Ic in acetonitrile •, Ic in 1,4-dioxane Δ, see Fig.1b) in homogeneous solutions point to a considerable contribution of the S-T_ transitions that proceed in the terms interaction zone into the observed CIDNP effect. The efficiency of such transitions increases with the solvent viscosity due to the increased residence time of the RP in the solvent cage.



Scheme1

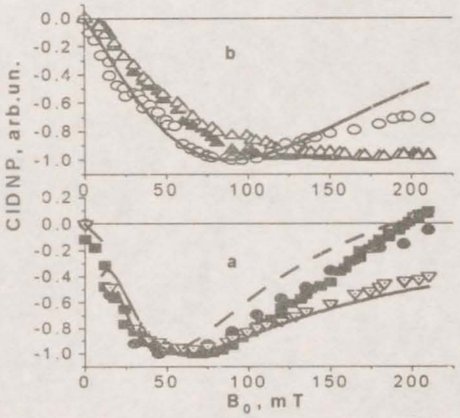


Fig.1

An analytical formula for the calculation of the CIDNP field dependences is proposed. It is based on a theoretical model that makes it possible to take into account the S-T_ transitions dependent on the exchange interaction, in the balance approximation. It provides qualitative agreement between the results calculated by this model and experimental evidence (Fig.1a, solid line - calculated for Ia in dioxane). However, the model has some drawbacks determined by the approximation employed, among which are the limitation in the value of J_0 and overestimation of the role of the $S\text{-}T_0$ transitions at short distances between the radicals. The experimental results are compared with calculated data obtained by the numerical solution of the stochastic Liouville equation [2]. The calculated and experimental field dependences are in satisfactory agreement (Fig.1a, dashed line - calculated for Ia in ether, Fig.1b, solid line - calculated for Ib in acetonitrile).

The ^{31}P-SNP spectra obtained in the photolysis of Ia and c are shown in Fig.2a and b, respectively.

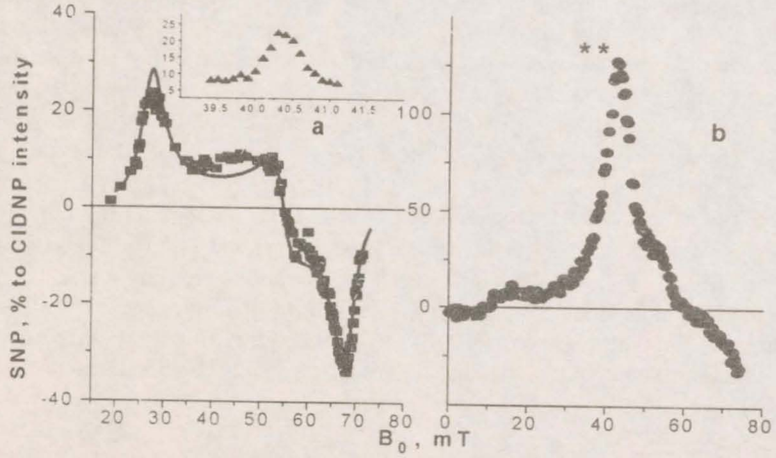


Fig.2

The analytical formula published in [3] was used for the theoretical treatment of the experimental spectra (Fig.2a, solid line).

It is shown that at low magnetic fields the significant polarization is induced by the influence of the resonance mw-field on free radicals. This polarization is formed due to the transitions

$C_1\alpha_e\beta_n + C_2\beta_e\alpha_n \rightarrow C_1\beta_e\alpha_n - C_2\alpha_e\beta_n$ (if $B_1 || B_0$, B_0=40.3mT, inset on Fig.2a),

$\beta_e\beta_n \rightarrow C_1\beta_e\alpha_n - C_2\alpha_e\beta_n$ (if $B_1 \perp B_0$, B_0=42.8mT, line ** on Fig.2b).

The time dependences for these lines were obtained and analyzed for different reaction products.

Acknowledgment. This work was kindly supported by INTAS (Project No 93-1626) and Russian Science Foundation (Project No 96-03-32930).

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POSTER 2

PHOTOIONIZATION OF N,N,N',N'–TETRAMETHYLPHENYLENEDIAMINE STUDIED BY Q–BAND TIME–RESOLVED EPR SPECTROSCOPY. SEPARATION OF SINGLET AND TRIPLET CHANNELS.

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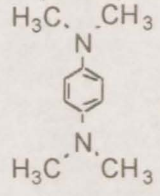
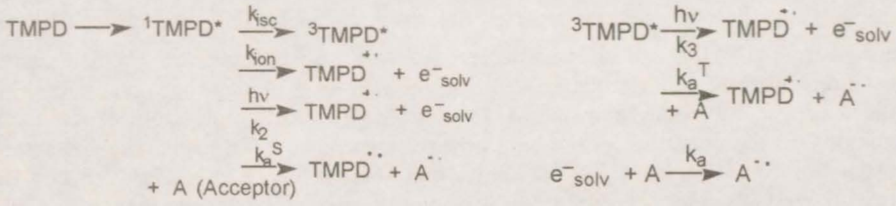
The photoionization of N,N,N',N'–tetramethylphenylenediamine (TMPD) in alcohols at room temperature was studied by time–resolved electron paramagnetic resonance (TREPR) spectroscopy at Q–band (35 GHz). The general opinion of most of the papers published in the past decade[1,2] is that photoionization of TMPD in liquid alcohols is monophotonic and proceeds predominantly through the singlet channel. But the extremely complex behavior of TMPD has led to conflicting reports concerning the spin multiplicity of the excited state precursor and the number of photons necessary for photoionization. The TREPR method can be very useful to clarify these problems. The scheme below summarizes the sequence of reactions leading to TMPD photoionization in liquid alcohols, including both triplet and singlet channels and reactions with acceptors.



TMPD



The spectra obtained in our experiments at short delay times (0.5 - 0.2 μs) contain a single emissive line and a broad part which along with the net emission has an E/A pattern. From spectral simulation we can assign the signal carriers to the $TMPD^{+\cdot}$ and e^-_{solv}. The $TMPD^{+\cdot}$ signal shows significant uncertainty broadening at this delay time, but careful simulations of later time delay spectra confirmed all hyperfine splittings to be equal to literature values for this radical ion. To confirm that the single line is due to e^-_{solv}, we performed the experiments using different quenchers and acceptors (N_2O, acetylene dicarboxylic acid, 2–bromo–2–methyl–propionic acid). The signals of $TMPD^{+\cdot}$ and e^-_{solv} both show net emission, which means polarization was created by the triplet mechanism (TM) in the excited triplet TMPD molecule and then transferred to both radicals. Experiments using 1,3-cyclohexadiene as a quencher also confirmed that the ion-radical pairs $TMPD^{+\cdot}$ and e^-_{solv} observed in the TREPR spectra arise from a triplet precursor. The sign of multiplet (E/A) polarization in $TMPD^{+\cdot}$ spectra unambiguously provided evidence for the negative exchange interaction J in these radical pairs (RP), contrary to work by Murai et al.[3] The RP's from the singlet channel, which are supposed to be dominant in this reaction,[1,2] do not appear in these TREPR spectra. The absolute value of the RPM polarization in singlet–born RP's might be small compared to that generated by triplet–born pairs, because of the generally shorter lifetime of the former ones. Using 2–bromo–2–methyl–propionic acid as electron acceptors the photoionization pathway through the excited singlet state was isolated. The TREPR signal at 0.1 μs shows presence of A/E multiplet polarization due to the singlet path way together with TM emissive polarization due to the triplet one. Spectra observed at later delay times show E/A multiplet polarization created in F–pairs of $TMPD^{+\cdot}$ and 2-methylpropionic acid-2-yl radical ($MPA^{\cdot}$). Analysis of that delay time behavior allowed us to conclude that J in the RP's of TMP and the $MPA^{\cdot}$ has a negative sign. Adding 1,3–cyclohexadiene as a triplet quencher allowed us to observe exclusively the singlet ionization channel. To determine if this pathway is biphotonic or monophotonic, measurements of the laser pulse energy dependence of the singlet polarization were performed. At low laser pulse energies, this curve shows approximately linear behavior. This result is in accord with the monophotonic ionization pathway in alcoholic solution that seems to be generally accepted in the most recent literature. Another feature of the curve is the saturation effect observed at a laser pulse energy of about 60 mJ. To determine whether photoionization through triplet channel is monophotonic or biphotonic, we have also measured the laser light dependence of the signal intensity of e^{-}_{solv} at the 0.05 μs delay time. The experimental curve shows nonlinear behavior at low pulse energies, and the beginning of signal saturation at very high pulse energies of about 200 mJ. To explain such large differences in behavior of these two curves we applied a kinetic scheme including all possible monophotonic and biphotonic ionization channels and also direct electron transfers from $^{1,3}TMPD^{*}$ to electron acceptors (see the scheme above). The successful simulations obtained confirm that i) TMPD photoionization though the triplet channel in liquid 2–propanol at room temperature is biphotonic if it occurs under our experimental conditions, ii) the saturation of the light intensity dependence for singlet channel can be explained only by the presence of biphotonic ionization at high enough laser power. The extent of monophotonic ionization from the singlet state is not ascertainable from our analysis. The fact that the obtained extinction coefficients $\varepsilon_{S1\text{-}Sn}$ and $\varepsilon_{T1\text{-}Tn}$ (at $\lambda = 308$ nm) come out to reasonable values gives us confidence in the self–consistency of our simple kinetic model. The consequences of exciplex formation and direct electron transfer from $^{1}TMPD^{*}$ to BMPA molecule rather than photoionization following by electron trapping in the singlet pathway are also discussed.

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POSTER 3

RELAXATIONAL PARAMETERS OF THE (PARATERPHENYLE)$^{-}$-(DIPHENYLESULFIDE)$^{+}$ RADICAL IONS OBTAINED BY THE OD ESR AND QUANTUM BEATS TECHNIQUES.

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The study of recombination fluorescence in the presence of a magnetic field yields unique information on short-lived radical ions forming under the radiolysis of hydrocarbon solutions of electron and holes acceptors. Recording of the fluorescence intensity when sweeping the external magnetic field under microwave pumping and stationary X-irradiation is referred to as the OD ESR technique [1]. The widths of the spectrum lines bear the information on the radical ions relaxation times [2]. In the so called quantum beats spectroscopy technique the kinetics of the fluorescence triggered by a pulse of ionizing radiation in the presence of an external magnetic field is monitored [3]. The spin relaxation leads to dumping of the kinetics oscillations resulting from singlet-triplet transitions in the pairs. This contribution reports a comparison of the (diphenylsulfide-d_{10})$^{+}$/(*p*-terphenyl-d_{14})$^{-}$ {(DPS)$^{+}$/(PTP)$^{-}$} radical ions relaxational parameters extracted from the OD ESR spectra and from quantum beats.

The OD ESR spectra of this radical ion pair in different hydrocarbons have two resolved lines, the low field one belonging to (DPS)$^{+}$ and the high field one to (PTP)$^{-}$. The lines splitting corresponds to the known [4] g-factor difference 0.0053±0.0002 of the radical ions. The widths of the lines, given in the table, show no dependence on the solvent viscosity and the temperature in the range -40 to+30 °C. The comparison of this values with the known hyperfine parameters [4] allowed to estimate the homogeneous part of the (DPS)$^{+}$ line width $K_{21}=(T_{2+})^{-1}+(T_{1-})^{-1}$ and the (PTP)$^{-}$ line width $K_{12}=(T_{1+})^{-1}+(T_{2-})^{-1}$, $T_{1\pm}$ and $T_{2\pm}$ being the longitudinal and transversal relaxation times, respectively. The frequencies of the quantum beats observed in the fields of 2400G, 4800G and 9600G correspond to the given g-factors difference. The beats amplitude decreases with time faster than would demand the known inhomogeneous width of an individual line, that allowed to obtain the impact of the transversal relaxation $K_{22}=(T_{2+})^{-1}+(T_{2-})^{-1}$ on the dumping of the oscillations (cf. the table). The extracted K_{22} values do not depend neither on the solvent viscosity nor on the magnetic field strength in the range 170 - 9600G.

The comparison of the ($K_{21}+K_{12}$) и K_{22} values demonstrates that the sum of all four reciprocal relaxation times exceed the sum of two reciprocal transversal relaxation times exactly two times. It means that in the studied range of the magnetic field the longitudinal and transversal relaxation times of the fast-relaxating radical ion (DPS) are equal $T_{1+}=T_{2+}$. This fact corresponds to the limiting case of the short correlation time of the relaxation process and accounts for the independence of the K_{22} parameter on the magnetic field.

Substance	ΔH_{pp}^{+},G	ΔH_{pp}^{-},G	K_{21}, 10^7 s^{-1}	K_{12}, 10^7 s^{-1}	K_{22}, 10^7 s^{-1}
n-Hexane	1.9±0.3	1.9±0.3	2.8±0.5	1.7±0.5	2.6±0.2
Isooctane	1.6±0.1	1.9±0.2	2.4±0.1	1.6±0.3	1.8±0.1
cis-decalin	1.3±0.1	2.0±0.1	2.0±0.1	1.7±0.3	1.8±0.1
Squalane	1.3±0.1	2.3±0.1	1.9±0.1	2.5±0.2	1.8±0.2

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POSTER 4

SPIN CATALYSIS: Theory

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Spin catalysis is a new phenomenon in spin chemistry which has been recently observed for radical reaction in a number of experiments rewiewed in [1,2]. For the initially triplet radical pair (R_1,R_2) this phenomenon appears as the increased recombinational yield if a third spin carrier - spin catalyzer - is present in a solution. Even in zero magnetic field spin catalyzers (stable radical R_3, biradical, triplet molecule, e.g. O_2, or paramagnetic ion M) induce the T-S conversion in a radical pair due to nonmagnetic interactions (spin exchange or spin pairing mechanisms [3,4]). The theory of the spin catalysis [5,6] is the theory of the spin evolution in multispin systems - radical triads (R_1,R_2,R_3) [7,8] or (R_1,R_2,M) [9] and includes irreversible processes: spin dependent geminate recombination and extracage reactions. In triads the T-S conversion of radical pairs is the part of doublet-doublet, triplet-triplet, etc., evolutions in multispin multilevel triads. For the three radical triad (R_1,R_2,R_3) the probability $\rho_{ss}^{T}(t)$ to find the initially triplet radical pair (R_1,R_2) in the singlet state is

$$\rho_{ss}^{T}(t) = (\Delta J \,/\, 2\Omega)^2\, Sin^2 \Omega t,$$

where $\Delta J = J_{13} - J_{23}$ is the exchange energy difference between the spin catalyzer R_3 and the radical pair partners R_1 and R_2. 2Ω is the doublet-doublet splittting. The condition $\Delta J \neq 0$ is the main one for the process of the spin catalysis. Neither doublet-doublet evolution of the triad, nor the singlet-triplet conversion of the radical pair are conceivable if $J_{13} = J_{23}$. The radical R_3, being the spin catalyzer for the triplet radical pairs, appears to be inhibitor for the unutually singlet pairs retarding the rate of the geminate recombination and decreasing the yield of the reaction product.

Kinetic equations for yields of spin catalized reactions have been derived. Conditions for spin catalysis, values of the catalytic effect, and the kinetic behavior are discussed. A new kind of quantum beats in chemical reactions is predicted.

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POSTER 5

CALCULATIONS OF EARTH-STRENGTH STEADY AND OSCILLATING MAGNETIC FIELD EFFECTS IN COENZYME B_{12} RADICAL PAIR SYSTEMS

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This poster uses EPR data for radical pair systems in several coenzyme B_{12} dependent enzymes and calculates effects of earth-strength steady and oscillating magnetic fields on their singlet-to-triplet yields via the radical pair mechanism. Energy level repulsions and the state-mixing they induce are found to be very important for determining overall sizes of effects and lower bounds on oscillating-field frequencies that can cause effects in such systems. B_{12} and similar systems with nearly axial zero-field spin Hamiltonians, dominated by terms over 100 times larger than Zeeman terms due to earth-strength steady fields, if under conditions of long lifetime, slow molecular tumbling, and slow spin relaxation, may be useful as biological sensors of both steady and oscillating fields that occur in nature, since the yields calculated show sensitivity to steady field strength (even after powder averaging) and orientation, and undergo steady-field-dependent shifts in the oscillating-field frequencies of maximal effect.

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Chem. Phys. 195 (1995) 59-69

J. M. Canfield, R. L. Belford and P. G. Debrunner, in press

POSTER 6

Influence of X-ray Irradiation and External Electric Field on the Magnetoplastic Effect in NaCl and LiF Crystals

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The influence of preliminary X-ray irradiation on the magnetoplastic effect is found out and investigated for NaCl and LiF single crystals. The dislocation mobility under the external static magnetic field B (in the absence of mechanical loading) has proved to be sensitive to rather weak X-ray irradiation (Mo, I=35 mA, V=45 kV) during t_r=5-60 sec [1]. Both the mean free path l of moving dislocations and their average density ρ_m decrease appreciably with the time of irradiation. In irradiated samples the measured values l and ρ_m linearly increase both in the time t_m of magnetic treatment (t = 2 -15 min) and in B^2 (B=0,2-0,7 T), the slopes of these dependencies decreasing with the doze of irradiation. Experiments in an alternating magnetic field created by a rotation of specimens in a static magnetic field were carried out. Two critical frequencies were found, above which the mean dislocation path l abruptly decreased (Fig.1). In NaCl(Ca) crystals the first critical frequency in the irradiated samples ($\nu_{c1}\cong$65 Hz, B=0,5 T) was twice more then that for the non-irradiated specimens. The second step on the l (ν) dependence at $\nu_{c2}\cong$150 Hz (B=0.5 T) was never observed without irradiation. After exposing irradiated crystals to the light of the tungsten lamp during one hour the second step disappeared and the position of the first one returned to the initial value ($\nu_c\cong$32 Hz). The specific features of the phenomenon were also studied for NaCl(Ni) and LiF (Mg) crystals. The change of the dislocation mobility in irradiated crystals, which especially clearly manifested itself in l (ν) dependencies, is apparently related to a generation of new magnetosensitive obstacles for dislocation motion and to the change of the state of initial paramagnetic centers provided by the irradiation.

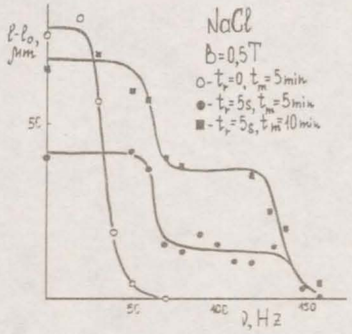

Fig.1

The strong influence of a weak external electric field (E=0.2-12 kV/m) under a magnetic field (B=0.05-0.3 T) on the dislocation mobility in NaCl and LIF crystals was found out and investigated [2,3]. It is essential that in the absence of a magnetic field even the highest of the electric fields used in our experiments did not bring to a dislocation motion. The electric influence is found only for edge (charged) dislocations and only when the **E** vector has a nonvanishing projection both on the slip plane and on the velocity of dislocation. No difference in the effect was observed at 300 K and 77 K. A mean dislocation path l and a density of moving dislocations ρ_m were experimentally studied as functions of various physical parameters. In particular, it was found that l =const$B^2t_m f(E)$ (Fig.2). The function f(E) starting from a quasi-linear increase in E comes to a constant value. The growth of *l* with B, E and t_m is usually changed by saturation at a level corresponding to an average distance between "forest" dislocations. However, at sufficiently high E there is no saturation and one can observe the transition from a relaxation of dislocation structure to a microcreep. Experiments in an alternative (over orientation) magnetic field have shown that at frequencies ν exceeding some critical value ν_c the path *l* abruptly decreases up to zero. The critical frequency $\nu_c \propto B^2$ proves to be insensitive to the electric field E.

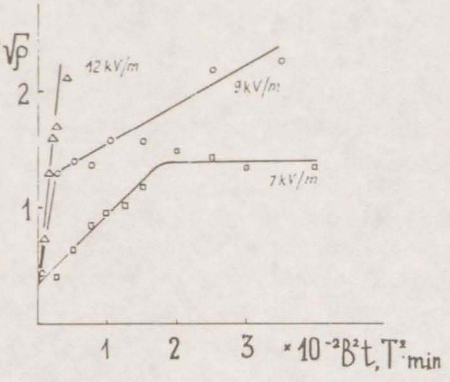

Fig.2

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POSTER 7

AUTOMATIC FREQUENCY CONTROL TO A SAMPLE CAVITY IN FOURIER TRANSFORM ELECTRON PARAMAGNETIC RESONANCE SPECTROMETER

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Time resolved electron paramagnetic resonance (EPR) spectroscopy has played a vital role in understanding the spin dynamics of organic free radicals. Whereas pulsed saturation recovery technique [1] provides insights into the mechanisms of spin relaxation, continuous-wave (CW) transient EPR [2] and Fourier transform EPR [3] techniques enable identification and observation of spin evolutions of transient radicals. Since their mode of detection of EPR signal is intrinsically different, a particular instrument is generally good for only one type of experiment. The detection of the EPR signal in the saturation recovery and transient EPR techniques, for example, is done in the presence of a low intensity microwave power, whereas in FT-EPR, the free induction decay (FID) is detected in the absence of such a power. The automatic frequency control (AFC) of the microwave in an FT-EPR spectrometer is therefore done to an external reference cavity, even though, AFC to a sample cavity is superior and is generally done in the other two techniques. Here we present a simple technique to do AFC to a sample cavity in a microwave bridge which can record FID as well as perform CW transient and saturation recovery experiments. The method relies on the fact that photolysing sources generally have repetition rates less than 100 Hz and the FID signals of the transient radicals so generated do no last longer than a few microseconds. Thus the FID's do not last longer than about 0.1% of the total time. So the microwave power reaching the sample cavity can be switched off during the detection of FID and the AFC error voltage can be held, by a sample-and-hold circuit, at its value just before the application of the microwave pulse. In the microwave circuit (Fig. 1), the PIN diode SPDT switch delivers a high power microwave pulse when at position 2, and a low power microwave at position 1 to the sample cavity for AFC and CW (steady state and

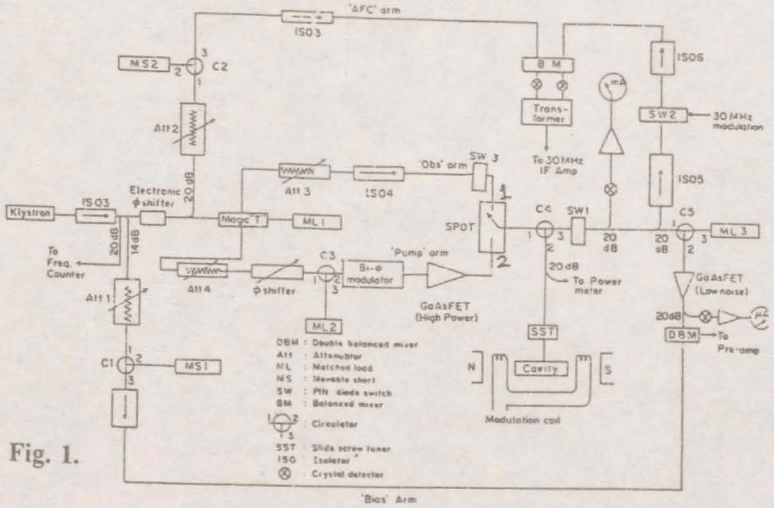

Fig. 1.

transient) signal detection. Another PIN diode switch (SW3) is used to block the CW power reaching the sample cavity during the detection of FID signal. With this arrangement, we recorded the FID signals (Fig. 2) at various values of the Zeeman magnetic field (B_0).

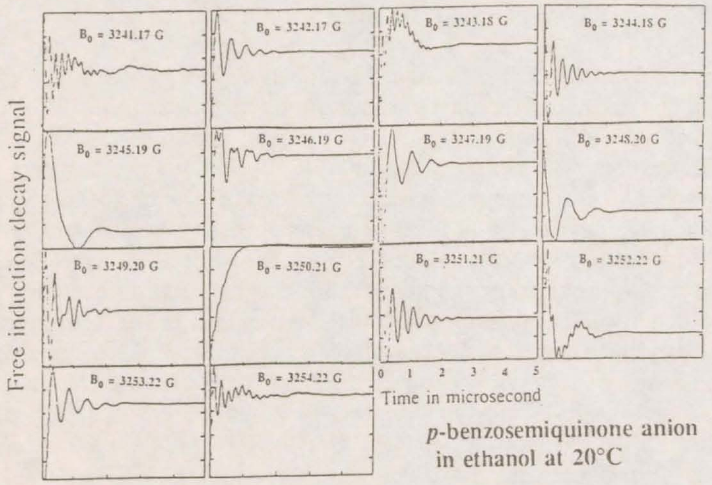

Fig. 2.

p-benzosemiquinone anion in ethanol at 20°C

Fig 3. shows the EPR signal obtained by Fourier transformation of the FID's. Since quadrature detection was not done, peaks with negative frequencies are folded over into the positive frequencies. The peaks marked with an arrow correspond to the EPR spectrum of the sample and match exactly with the CW spectrum shown in the inset.

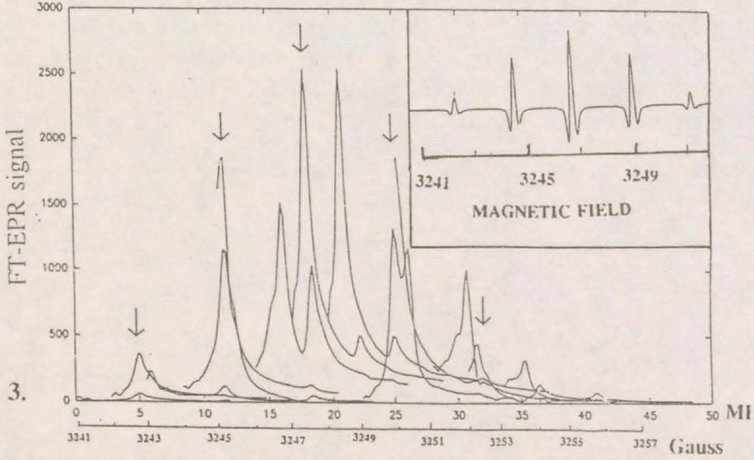

Fig. 3.

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POSTER 8

LOW AND ZERO FIELD STIMULATED NUCLEAR POLARIZATION IN CYCLIC KETONES

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The stimulated nuclear polarization (SNP) phenomenon in biradical reactions is experimentally well investigated and theoretically described in the case of relatively strong external magnetic fields, $B_0 >> 2|J|$ and at $B_0 \sim 2|J|$, where J is the exchange coupling [1]. In both cases SNP formation can be qualitatively understood using a scheme of energy levels and considering the electron spin transitions in the triplet manifold induced by the radio frequency (rf) irradiation [1]. In low B_0 field there is no simple picture of how SNP is created. The calculation of SNP of short lived radical pairs in weak and zero magnetic field predicts a significant non-zero SNP effect at zero external field B_0 for some favourable sets of parameters [2]. In this contribution we report on the observation and qualitative analysis of the considerable ^{13}C SNP at low-field $B_0 < hfi$ for acyl-alkyl biradicals, which are formed by α-bond cleavage in a cyclic ketones in the excited triplet state.

The ^{13}C SNP experiments were performed on a custom-built FT NMR spectrometer (7 T) with a fast magnetic field cycling using of a pneumatic probe transfer system. A solution of 0.06 M of cyclo-undecanone (with ^{13}C at natural abundance) in chloroform was irradiated by a Lambda-Physik excimer laser at 308 nm. The frequency for pumping of electron spin transitions was 75, 300 and 400 MHz. After irradiation at low field the sample was transferred into the cryomagnet of the spectrometer, where the ^{13}C or ^{1}H NMR spectra of the polarized products were detected at a frequency of 75 MHz and 300 MHz, respectively.

In acyl-alkyl biradicals the carbonyl-^{13}C exhibit the largest scalar hyperfine coupling constants of 12 mT. Hfi constants of α-carbons are 4.5 mT and 4.0 mT for acyl and alkyl end, respectively. The figure shows the experimental ^{13}C CIDNP dependence on magnetic field B_0 in cycloundecanone for different carbon positions without rf pumping and in the presence of rf irradiation at a frequency of 300 MHz. For both carbon positions a SNP effect of the considerable size is detected. The carbonyl

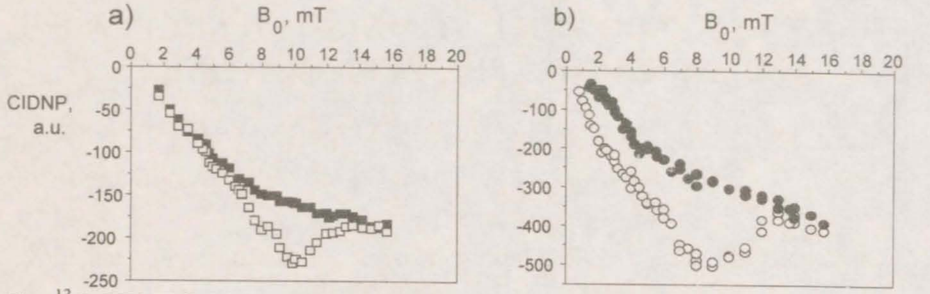

Fig. ^{13}C CIDNP field dependence in cycloundecanone without (solid symbols) and with 300 MHz rf pumping (open symbols): a) α carbons; b) carbonyl carbons. B_1=1.2 mT.

^{13}C exhibit at low field a much strong SNP than the α-carbons. The strong SNP effect at low field for the carbonyl-carbons can be related to the large hfi constant of this position, which is comparable with the pumping frequency. This size of hfi can, in principle, lead to a redistribution of the contributions of different channels of intersystem conversion in low field. At lower pumping frequency (75 MHz) qualitatively similar effects are observed also for nuclei with small hfi-constant: α- and β-protons and α-carbons. Increasing the pumping frequency to 400 MHz leads to a slight suppression of the low field wing in the carbonyl-^{13}C SNP spectrum.

The strong non-zero SNP at very low B_0 is a rather surprising effect. Note that at B_0=0 the radical pair mechanism cannot lead to any polarisation in the reaction product due to the symmetry of spin interaction, and hence CIDNP vanishes. A qualitative analysis using a perturbation approach gives for the case of short lived RP the result that for a circularly polarized rf field the SNP at zero B_0 is non-zero and proportional to $A^3\omega\, B_1^2 \langle S_{Az}S_{Bz}\rangle|_{t=0} \cdot t^6$.

For quantitative analysis we used the phenomenological two-state model (see, e.g., [3]). We found that the SNP line shape for α-carbons with small hfi constant is rather insensitive to the rate of the non-spinselective biradical decay process and can be fitted well for a broad range of values for this rate. In contrast, satisfactory agreement with the experimental data for the carbonyl-carbons can be achieved only for considerably high rates for that process of at least 10^7 s^{-1}.

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POSTER 9

MODEL FOR MAGNETIC FIELD EFFECTS ON RADICAL PAIR RECOMBINATION IN ENZYME KINETICS

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OBJECTIVE: Recent experimental studies have shown magnetic field effects on coenzyme B12-dependent ethanolamine ammonia lyase activity in vitro (Harkins and Grissom, Science 263, 958 (1994)). The magnetic field modulates the recombination kinetics of a transient pair of free radicals that is formed within the enzyme reaction cycle (radical-pair-mechanism, RPM). We present a prototypic model for describing magnetic field effects in enzyme reactions in accord with the RPM. METHODS: The enzyme model consists of an extended Michaelis-Menten reaction scheme including an intermediate enzyme-substrate complex where a spin-correlated radical pair exists. The simple structure of the scheme enables calculating the enzyme reaction rate explicitly by combining chemical kinetics with magnetic field-dependent spin kinetics. Radical pair-recombination probability is determined by using the exponential model. RESULTS: Calculations show that the size of the magnetic field effect depends on relations between different rate constants, such as (i) the ratio between radical pair-lifetime and the rate of magnetic field-sensitive singlet-triplet intersystem crossing, kisc, induced by the hyperfine interaction - and the Dg - mechanisms, and (ii) the chemical rate constants of the enzyme reaction cycle. An amplification factor that is derived from the specific relations between the rate constants is defined. It accounts for the fact that while the magnetic field-induced change in radical pair recombination probability is very small (1 %) the effect on the reaction rate of the enzyme is considerably larger, for example, by a factor of 1...100. The model reproduces experimental results on magnetic field effects on ammonia lyase activity (see OBJECTIVE) that revealed a reduction in Vmax / KM at low flux densities (- 25 % at 100 mT) and an increase at high flux densities (> 180 mT). DISCUSSION: The simulations demonstrate that both the hyperfine interaction - and the Dg - mechanism contribute to the observed magnetic field-dependence of ammonia lyase activity. Our calculations reveal that the enzyme reaction cycle exhibits an intrinsic capability for amplifying small initial changes in radical pair-recombination probability. This behavior results from combining magnetic field-dependent spin kinetics, which is on the nanosecond time-scale, and chemical kinetics of the enzyme processes, which are several orders of magnitude slower. Consequently, a 1 % change in radical pair-recombination probability, for example, can result in a 25 % reduction in enzyme activity. This shows that interpretation of the experimental results on ammonia lyase activity has to be based on both the radical pair mechanism as a primary coupling mechanism of the magnetic field and on the secondary biological change related to enzyme kinetics.

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POSTER 10

TIME-RESOLVED RYDMR IN THE INTRA- AND INTERMOLECULAR CHARGE-TRANSFER REACTION BETWEEN PHENANTHRENE AND *N,N*- DIMETHYLANILINE

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Reaction Yield Detected Magnetic Resonance (RYDMR) is a powerful technique to investigate the spin correlation of the radical pair. In this presentation we apply RYDMR spectroscopy developed by McLauchalan et al. [1] to the intra- and intermolecular electron transfer reaction between *N,N*-dimethylaniline and phenanthrene for polymethylene-linked and non-linked systems, respectively.

Time profile of RYDMR signals (microwave effect on exciplex fluorescence) and the exciplex fluorescence for the polymethylene-linked and non-linked systems is shown in Figure 1. The RYDMR signals for linked and non-linked systems are almost the same, even though the exciplex fluorescence in linked system decays faster than that in non-linked system. These results indicate that the lifetime of the radical ion pair is longer for the linked system than that for the non-linked system.

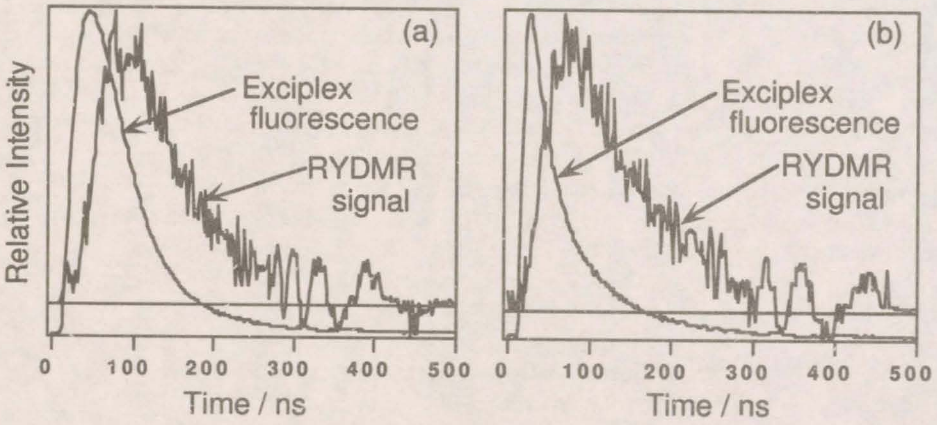

Figure 1. Comparison of the time profile of RYDMR signals at the resonance field and the exciplex fluorescence between non-linked (a) and linked (b) system of phenanthrene and *N,N*-dimethylaniline.

Figure 2 shows RYDMR B_0 spectra for the linked and non-linked systems. The spectrum for the linked system is remarkably broader compared with that for the non-linked system (spectral linewidth for linked system is almost twice as large as that in the non-linked system). This broadening leads us to conclution that the exchange interaction J is more effective in the linked system than in the non-linked system. To further substantiate this conclution, the dependence of the microwave effect on both chain length and solvent permittivity in linked system is discussed. The theoretical models to interpret the difference of the microwave effect between two systems are now in progress.

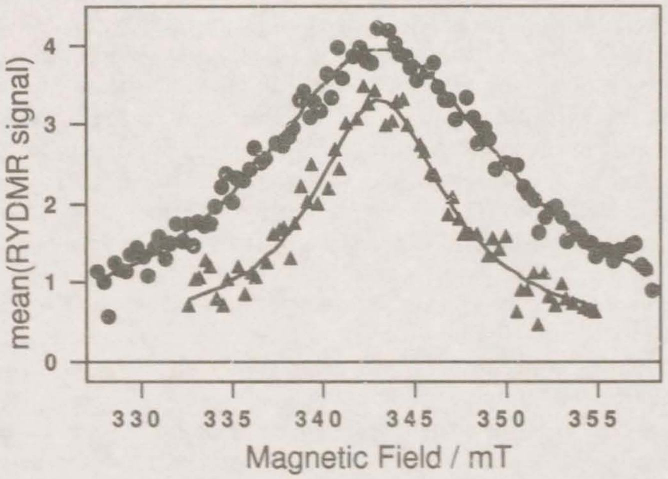

Figure 2. RYDMR B_0 spectra for polymethylene-linked (circles) and non-linked (triangles) system of phenanthrene and *N,N*-dimethylaniline. Averaging period is 80 -140ns after flash

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POSTER 11

LIGAND DEPENDENCE OF ELECTRON SPIN RELAXATION IN Fe(III) COMPLEXES STUDIED BY PARAMAGNETIC NMR

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In spin chemical studies carried out at this laboratory, low spin complexes of Ru and Fe with d^5 electron configuration and Kramers doublet ground states have figured prominently as "d-electron radicals ". Since their magnetic properties deviate considerably from those of typical organic radicals it was necessary to develop a specific d-electron radical pair spin chemistry [1], [2]. As was concluded from the analysis of the observed magnetic field effects, and has been independently confirmed by $^1H - NMR$ of the paramagnetic complexes, very short electron spin relaxation times τ_s on the order of 10 ps are characteristic of these compounds. In the literature there seem to be only few attempts at giving a quantitative mechanistic account of such fast spin relaxation for Kramers doublet systems in liquid solution. Therefore, in order to learn more about the mechanistic details and the structural dependence of electron spin relaxation in such systems of spin chemical interest we studied the temperature dependence of τ_s in solutions of the following complexes with mixed ligand spheres: $[Fe(bpy)_3]^{+++}$, $[Fe(bpy)_2(CN)_2]^+$, and $[Fe(bpy)(CN)_4]^-$. Our experimental determination of τ_s was based on measurements of $^1H - T_1$ times with a 400 MHz NMR spectrometer employing the usual inversion recovery pulse sequence. The observed $^1H - T_1$ times were related to τ_s by using a generalized Solomon-Morgan-Bloembergen equation given by Bertini et al. [3]. Results obtained at room temperature are given in table 1.

complex	solvent	τ_s [psec]
$[Fe(bpy)_3](PF_6)_3$	D_2SO_4	13.80
$[Fe(bpy)_3](PF_6)_3$	CD_3CN	10.19
$[Fe(bpy)_2(CN)_2]PF_6$	CD_3CN	6.05
$[Fe(bpy)_2(CN)_2]NO_3$	D_2O	4.86
$Na[Fe(bpy)(CN)_4]$	D_2O	2.49
$H[Fe(bpy)(CN)_4]$	D_2O	2.85
$H[Fe(bpy)(CN)_4]$	CD_3OD	3.18

Table 1: Electron spin relaxation times determined at 293 K

These data show that a clear structural correlation exists. Replacing bipyridine by cyano ligands leads to a reduction of the spin relaxation time.

The temperature dependence of τ_s is shown in Figure 1. It exhibits an Arrhenius-type behaviour suggesting an Orbach mechanism whereby spin relaxation within the lowest Kramers doublets is achieved through direct thermal excitations of the nearest electronically excited states.

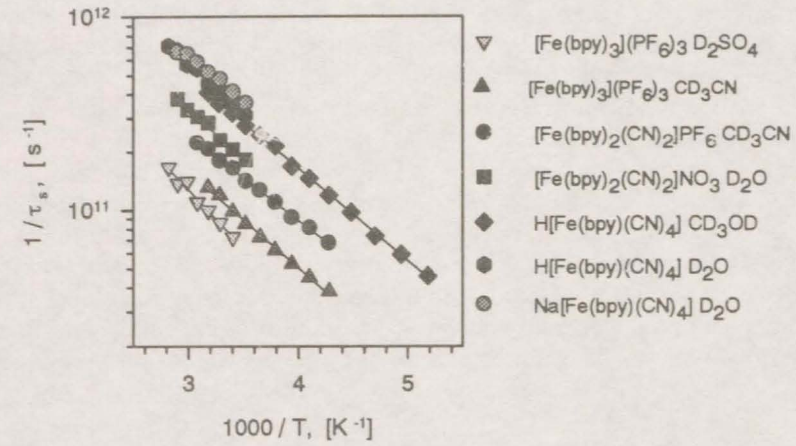

Figure 1: Temperature dependence of electron spin relaxation time

The results will be discussed in the light of Kivelson's [4] adaptations of well known solid state spin relaxation mechanisms to the situation in liquid solution. Implications regarding the values of specific parameters of the theory will be critically examined with respect to the properties of the systems investigated.

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POSTER 12

SPIN CHEMISTRY WITH FERROCENES

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Magnetic properties of paramagnetic transition metal complexes ("d-electron-radicals") are largely determined by d-electron configuration, ligand field strength, symmetry and by spin-orbit coupling. Extending our previous spin chemical investigation with $\mathrm{Ru^{III}}$-trisbipyridyl type complexes, characterized as d^5 electron systems in distorted octahedral fields, we have now turned to the spin chemistry of ferricenium systems [1], whose electronic properties are characteristic of a d^5 electron configuration in a ligand field of D_5 symmetry causing a different ordering of the d-orbitals than in the former case.
Following work by Tamura et al. [2] who had investigated the ΔG_{bet} dependence of the free radical formation efficiency η_{ce} in these systems, radical pairs involving a ferricenium ion as a d-electron radical were produced from ferrocene and some of its derivatives by oxidizing them with photogenerated triplets of methylene blue. The reaction scheme is as follows:

$$ {}^3\mathrm{MB}^+ + [\mathrm{FcR}] \xrightarrow{k_q} {}^3({}^2\mathrm{MB}^\bullet \cdots {}^2[\mathrm{FcR}]^+) \begin{array}{l} \xrightarrow{k_{\mathrm{ce}}} {}^2\mathrm{MB}^\bullet + {}^2[\mathrm{FcR}]^+ \\ \xrightarrow{p_{\mathrm{s,i}} k_{\mathrm{bet}}} {}^1(\mathrm{MB}^+ \cdots [\mathrm{FcR}]) \end{array} $$

The radical pair originates with triplet spin and decays by cage escape (k_{ce}) and geminate backward electron transfer which is subject to a spin selection rule because it regenerates the ground state of reactants where all spins are paired. This selection rule is implemented by expressing the rate constants of backward electron transfer as a product of effective singlet character $p_{\mathrm{s,i}}$ of the respective spin substate i of the radical pair and a rate constant k_{bet} corresponding to a fully spin allowed process. Due to the differences in the $p_{\mathrm{s,i}}$ the magnetic field dependent repopulation kinetics of the radical pair spin substates affects the cage escape efficiency η_{ce} which thus becomes magnetic field dependent, too.
We examined the magnetic field dependence of η_{ce} in a field range from 0 to 3.2 Tesla using ns-laser flash spectroscopy. The magnetic field dependence, depicted in Figure 1 exhibits a monotonic decreace of η_{ce}. It is not yet saturated at 3.2 Tesla. The size of the effects is sensitive for the substituents at the Cp rings. The field dependence can be simulated using a previously [3, 4] described spin chemical model and taking into account the specific electronic properties of ferricenium cations as known from ESR investigations. From the simulations we determined the rate parameters k_{ce}, k_{bet} and τ_s (the spin relaxation time of the ferrocenium cation). The results are shown in Table 1. In contrast to the interpretation of Tamura et al. [2] who assigned the observed trend in η_{ce} to a systematic change of k_{ce} througout the series, our spin chemical results indicate very remarkable changes in the rate constant k_{bet} of backward electron transfer, which in some of these systems apparently reaches extremely high values.

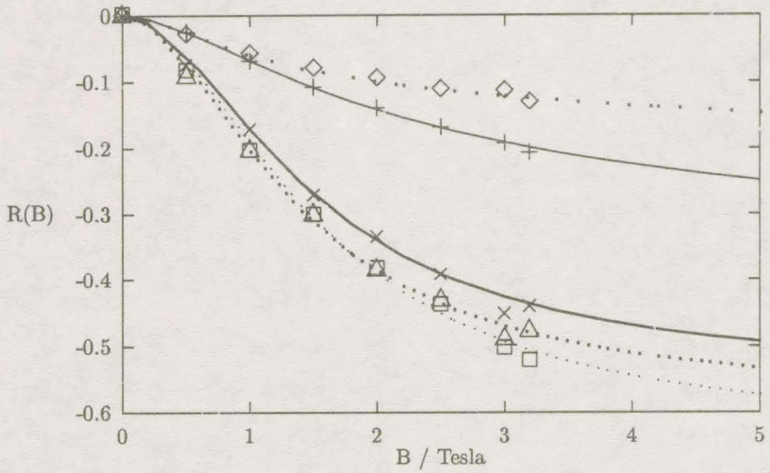

Figure 1: Magnetic field effect R(B) on η_{CE} for ◇ Fc-OMe, + Fc, × FC-COMe, □ Fc-COOH and △ Fc-CN. The lines correspond to the theoretical simulations as described in the text.

FcR	ΔG_{BET}	η_{CE}	k_{CE}	k_{BET}	τ_s
	eV	%	$\mathrm{ns^{-1}}$		ps
Fc-OMe	-0.63	32.0	5	65	1.2
Fc	-0.70	21.0	15	605	6.5
Fc-COMe	-0.94	6.7	7	13400	6.8
Fc-COOH	-0.94	6.4	6	17800	8.1
Fc-CN	-1.06	3.9	3.5	13300	7.8

Table 1: Reaction parameters ΔG_{bet} and η_{ce} according to ref. [2] and rate parameters k_{ce}, k_{bet} and τ_s determined by spin chemistry.

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POSTER 13

THE MANIFESTATION OF DEGENERATE ELECTRON EXCHANGE IN SNP AT HIGH MAGNETIC FIELDS.

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The processes of degenerate electron exchange (DEE) in radical-ion reactions have a significant influence on the spin dynamics of radical ion pairs (RIPs) and free radical ions. The spectra of stimulated nuclear polarization (SNP) [1] are determined by the spin dynamics in RIPs and, consequently, are affected substantially by the DEE. The influence of the DEE on the SNP spectra has been investigated qualitatively [2]. It is shown that the DEE mainly affects the intensity of SNP, while the shapes of the SNP spectra remain the same in a wide region of DEE rates. In this work we performed a detailed theoretical and experimental investigation of the DEE effect on the SNP intensity and spectra under the spin-locking conditions at high magnetic fields ($B_o >> A$, where A is HFS constant).

The theoretical description of DEE processes is performed in two different ways: the analytical solution for simple two-site model and the numerical solution of equations for noncorrelated frequency migration. The first approach allows one to obtain an analytical formula for the dependence of the SNP intensity on the rate of DEE at low mw-field amplitudes ($B_1 << A$) and low DEE rates ($A\tau_e >> 1$, τ_e is the time of DEE). For the RPs with a few magnetic nuclei, the DEE effect on the shape of SNP spectra in a wide region of high mw-amplitudes was investigated using the numerical solution of equations for noncorrelated frequency migration. It is shown that the DEE weakly affects the splitting in SNP spectra due to the difference in the sign of spectral SNP components (in contrary to the significant influence of DEE on the splitting in ESR and RYDMR spectra).

The influence of DEE on the intensity and shape of SNP spectra was investigated in the model reaction of photosensitized *cis-trans*-isomerisation of fumaronitrile (FN) with naphthalene (Naph) in CD_3CN. The experimental results and theoretical predictions were compared. The experimental setup was described in detail in [1].

The authors thank The Russian Foundation for Basic Research, Grant N^0 96-03-32930, and INTAS, Project N^0 93-1626, for financial support.

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POSTER 14

ELECTRONIC AND COMPUTER DESIGN OF NANOSECOND LASER FLASH PHOTOLYSIS

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Laser flash photolysis is the basic and most informative method to study photochemical reactions. However, to obtain high sensitivity, the use of serial blocks, produced by firms is ineffective and a specialized electronic equipment should be made directly for flash photolysis. The main problem is to create the wideband unoverloading amplifier to obtain high sensitivity in nanosecond time range. One of the problems is to remove the pedestal of probe light pulse from a signal, which arrives at the analog-digital converter (transient digitizer). An important problem is the stability and reproducibility of the flat top of a probe pulse, which determines the sensitivity in measurements in micro and millicecond time ranges. In high precision experiments the exact measurement of laser pulse intensity is necessary. An important moment is also the creation of convenient and multitarget software of installation work.

Our group over a period of years has developed the installations of nanosecond laser flash photolysis with an excimer XeCl laser (wavelength 308 nm, energy 50 mJ, pulse duration 10 ns). One of the last installations has the sensitivity by optical absorption of about 10^{-4} per pulse with time resolution 10 ns and works under the control of an IBM PC computer. To achieve the high metrological characteristics a number of original blocks were developed briefly described below .

1. A xenon DKSh-150 (or CSX-150, LX-150) lamp is used as the source of probe light. The pulse has a flat top of 2 ms duration. A part of radiation is branched off to photodiode, the signal of which is used as the signal of feedback. It permits one to achieve instability of the flat top no less than 10^{-3} with the charge current up to 150 A and pulse power 10 kW.

2. The unoverloading amplifier with probe light signal compensation at input and the digital measurement of probe light intensity with the accuracy of compensation no less than 2.5×10^{-4}. It permits one to detect and amplify a weak optical absorption signal on the pedestal of a more powerful probe light pulse. A band of frequencies is no less than 250 MHz with the gain of 50. The compensation of a probe light signal is executed by analog-digital way directly before a laser pulse. The accuracy of intensity probe light measurement is about 0.025 %. (12 bit). The availability of compensation permits one to have an effective (without of the compensation) 16-bit resolution with a 10-bit transient digitizer.

3. The 10-bit transient digitizer with a sampling speed from 10 ns/point and the memory of 65535 points with high dynamic characteristics. It permits one to detect millisecond signals with the nanosecond resolution and to process with high accuracy.

4. The multifunctional programmed timer, including 6 time channels with advanced logic of start. A timer permits one to generate any time pulse diagram of 6 pulses with a step of 10 ns stabilized by quartz.

5. The unit of energy laser pulse measurement with simultaneous reception of time mark. Using one photodiode we solve two problems, such as the energy laser pulse measurements with accuracy of about 0.025 %, and the determination of time pulse generation with time jitters less than 10 ns. In spite of the fact that these problems present essentially different requirements on signal processing (first, it is necessary to execute the complete charge tax from photodiode (integration), and second, to determine the minimum time increase (differentiation)), both problems are decided with one device.

6. The crate-controller for serial high-speed channel of CAMAC connection with IBM PC compatible computer. The controller has a galvanic crate isolation from computer to reduction noise from a computer pulse supply.

For experiments and processing of kinetic results the software package WinFotol is developed in Borland Pascal for Windows which works under the control of Windows 3.11 or Windows 95 systems. The program WinFotolSetUp permits one to conduct the set-up of experimental conditions in a dialogue mode. These conditions include the times of the opening laser and probe pulses shields, the determination of the positions of separate units in CAMAC-crate, the determination of pulse sequence in experiments (pulse for noise registration, measuring pulse, pulse for the determination of base line and pulse, during which the contribution of luminescence is determined for its subsequent subtraction in registration of absorption signal).

The program WinFotolMain permits one to establish a type of experiment (registration of absorption, luminescence or magnetic effect), time resolution, number of storages and the time between pulses, which permits one to mix a solution in cuvette. Shooting can be performed to determine the necessary amplification coefficient and the slit width of monochromator. After experiments the monitor screen shows the kinetics of the signal of either absorption or luminescence and a wide set of the menu, enabling one to choose readily the range of processing, prospective zero level and kinetic law. The chosen algorithms permit one to quickly process the kinetics even according to the complex kinetic laws and to receive amplitudes and rate constants.

The window "Information" permits one to record the experimental conditions (molecule, solvent, concentration, number of storage, wavelength of registration, energy of laser and probe pulses, comments). In the "Transactions" window it is possible to separately examine all accumulated kineticses and to exclude those containing a strong signal noise. Record of kinetics and complete experimental information is carried out in file with the .dat expansion or in ASCII codes (file with .asc expansion) which permits to easily transmit the data to the modern graphic editors as Origin, MatLab for representation of results.

POSTER 15

"CIDEP in Radical-Singlet Molecular Oxygen System"

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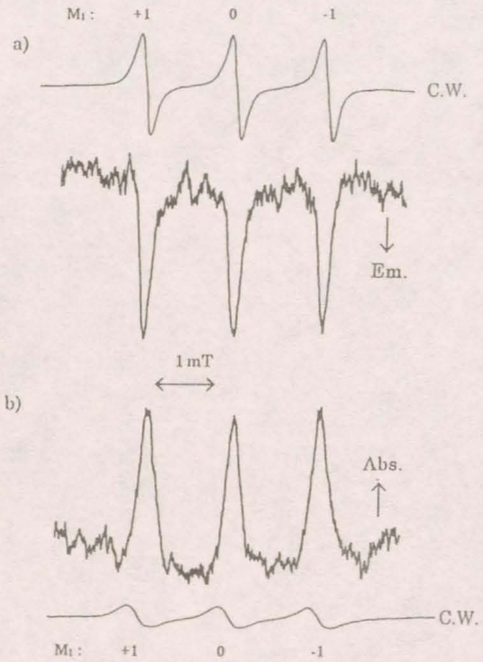
Radical-triplet pair mechanism (RTPM) for CIDEP generation is studied in singlet-radical system. Especially, we will report CIDEP generation in radical-singlet molecular oxygen system. Figure 1 shows CIDEP spectrum of tetramethylpiperidylnitroxy (TEMPO) measured in 308 nm laser photolysis of anthracene-TEMPO system in benzene at 300 K in a) degassed condition and b) air-saturated condition. The gate was opened from 1.5 to 2.0 μs. The line width of TEMPO was slightly larger than that in degassed solution. The broadening of the line is probably due to dissolved molecular oxygen. It is noteworthy that TEMPO shows net absorptive or emissive signals depending on the systems. Previously, we reported[1] that net emissive signal of TEMPO in anthracene-TEMPO system was due to RTPM with quartet precursor. However, this mechanism is not responsible for net absorptive signal in air-saturated condition. Since the only difference between the two is the concentration of molecular oxygen dissolved in the solution, it is considered that molecular oxygen is responsible for the generation of absorptive signal of TEMPO.

In air-saturated system, 308 nm laser excites anthracene to singlet excited state which is subsequently quenched by the molecular oxygen in the solution to produce singlet molecular oxygen. Because of this quenching process, the yield of triplet anthracene is more than ten times smaller in air-saturated condition than that in degassed condition. Thus, it is reasonable that no emissive signal was observed in air saturated condition. After $^1O_2$ was produced, TEMPO deactivates $^1O_2$ to produce ground state O_2. In this process, it is expected that the total spin angular momentum is preserved to produce TEMPO-triplet O_2 pair with doublet state. According to the RTPM with doublet precursor[2], free radical should show net absorptive CIDEP signal. Therefore, observed net absorptive CIDEP of TEMPO in $^1O_2$-TEMPO system is explained by RTPM with doublet precursor.



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POSTER 16

The Solution of a Statistical Model of Radical Recombination in Magnetic Field

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We investigated the stochastic model of radical recombination in the presence of magnetic field. The model consists of Δg mechanism

$$\mathcal{H} = \omega\left(|T_0\rangle\langle S| + |S\rangle\langle T_0|\right) \tag{1}$$

and recombination reantion and diffusion process of relative distance of the radical pair.

The stochatic Liouville equation for the density matrix ρ is

$$\frac{\partial\rho}{\partial t} = -i[\mathcal{H},\rho] + D\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial\rho}{\partial r} \tag{2}$$

with the boundary condition

$$D\frac{\partial\rho}{\partial r}\bigg|_{r=R} = \frac{h}{2}(\mathcal{P}_S\rho + \rho\mathcal{P}_S)\bigg|_{r=R} \tag{3}$$

In order to deal with this problem analytically, we introduce $\rho = \frac{\sigma}{r}$ and the spatial variable $x = r - R$. the we have

$$\frac{\partial\sigma}{\partial t} = -i[\mathcal{H},\sigma] + D\frac{\partial^2\sigma}{\partial x^2} \tag{4}$$

We may perform Laplace transforms in space

$$\hat{\sigma}(k,t) = \int_0^\infty e^{-ikx}\sigma(x,t)dx \tag{5}$$

and time

$$\hat{\sigma}(k,z) = \int_0^\infty e^{-zt}\hat{\sigma}(k,t)dt \tag{6}$$

The initial condition is written as

$$\sigma(x,t=0) = \frac{1}{4\pi r_0}\delta(x + R - r_0)\left(p_S|S\rangle\langle S| + p_{T_0}|T_0\rangle\langle T_0|\right) \tag{7}$$

where r_0 is the initial distance and p_S, p_{T_0} are initial probabilities of singlet and triplet pairs. The recombination rate is defined by

$$P_r = 4\pi R \lim_{z\to 0} \sigma_{SS}(0^+, z) \tag{8}$$

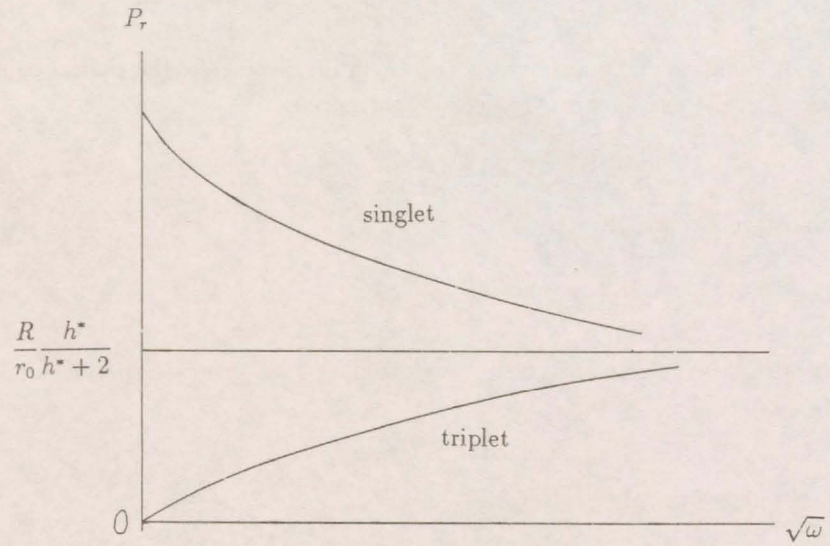
The analysis for small z gives P_r as a function of the field ω. In the high magnetic field limit, we have

$$\lim_{\omega\to\infty} P_r = \frac{R}{r_0}\frac{h^*}{h^*+2} \tag{9}$$

where $h^* = Rh/D$. In the low field limit,

$$P_r = \left(\frac{R}{r_0}\right)\frac{h^*}{1+h^*}\left[p_S - \frac{R\sqrt{\omega}}{2\sqrt{D}}\left(\frac{r_0}{R}(p_S - p_{T_0}) + \frac{h^*}{1+h^*}p_S\right) + \cdots\right] \tag{10}$$

The square root dependence on the magnetic field was observed experimentally.



POSTER 17

SPIN-POLARIZED EPR SIGNAL OF THE PRIMARY RADICAL PAIR OF BACTERIAL PHOTOSYNTHESIS. M(Y)210W MUTANT OF *RB.SPHAEROIDES*: EVIDENCE FOR DISTRIBUTION OF THE RADICAL PAIR PROPERTIES

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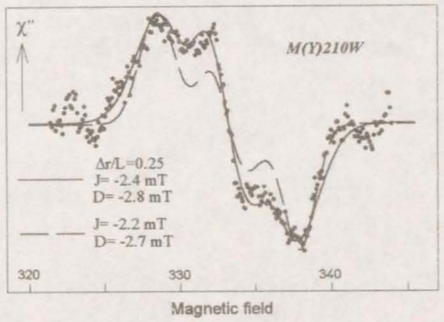
Using flash-EPR spectroscopy we detected spin-polarised signals of the primary radical pair P^+I^- (RP1) in a number of photosynthetic bacteria [Proskuryakov et al., these Proceedings]. Here we report on simulation of the RP1 spectrum of *Rb.sphaeroides* mutant M(Y)210W using the theory of spin-correlated radical pairs [1]. For a given orientation of the radical pair in the external magnetic field a stick spectrum was calculated and convolved with an appropriate lineshape. Then it was summed over all possible orientations. The g-tensors of P^+ and I^- were assumed to be isotropic and fixed to their literature values.



Experimental EPR spectrum of RP1 in reaction centers of M(Y)210W mutant of *Rb. sphaeroides*, measured at 70K (dots). Smooth lines show the simulated spectra, calculated within the framework of the two models. Dashed line stands for best fit when linewidths of separate radicals are determined by the RP1 lifetime (model 1). The solid line represents the best fit in case of the model 2 with distribution of exchange interactions between the components of RP1. The best-fit parameters are given in the figure. Δr stands for the width of normal distribution.

In fitting, we utilized two different models for describing the RC properties:

1. The RC structure is fixed, with the distance between P^+ and I^- constant. The free parameters of this model were spin dipolar interaction D, exchange interaction J, and linewidths ΔBpp of both radicals. Due to the fast recombination of RP1, one has to introduce sufficient lifetime-broadening, so that ΔBpp is obtained by convolution of the steady-state linewidths and this broadening factor. The figure shows that this approach does not lead to a satisfactory agreement.
2. The RC properties experience distribution. In calculations, we introduced normal distribution of the radical separation *r* in RP1. The largest effect of such variation will be on the exchange, so J was the only distributed parameter. To translate the distribution of separations into the changes in J, we used the relation J~exp(-2*r*/L), where L depends on the properties of inter-radical medium [2]. The figure shows that this approach results in a much better correspondence with the experimental spectrum. Thus, we conclude that distribution of parameters should be taken into account for such strongly-interacting species, as RP1. Financial support of NWO and INTAS is gratefully acknowledged.

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2. 2. G. I. Likhtenstein, A. I. Kotel'nikov, A. V. Kulikov, Doklady AN SSSR, 257 (1981), 733

POSTER 18

RECOMBINATION OF THE RADICAL PAIRS UNDER THE FLUCTUATING MAGNETIC FIELDS

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An experimentalist studying the spin and magnetic field effects in the recombination of radical pairs usually believes that he can control the magnetic fields in the system. However, in addition to the external magnetic field *B*, the electron spin of a radical can also experience the fluctuations of the magnetic field. Such fluctuations can be effectively caused by the random rotation of a radical with an anisotropic hfi or g-factor.

In the present work we have investigated the influence of the fluctuations of the magnetic field on the radical pair recombination in the high-field case (*B* >> hfi), where only the transitions between singlet (S) and triplet (T_o) states are important.

In our calculations, we have employed the exponential model. The behaviour of the radical pair is described by the stochastic Liouville equation for the spin density matrix $\rho(\omega,t)$:

$$\partial_t \rho(\omega,t) = \hat{L}\rho = -\mathrm{i}(\omega_o + \omega)\hat{H}_o^x\rho + \gamma\partial_\omega\left(\omega + \Delta^2\partial_\omega\right)\rho - \kappa\rho \qquad (1)$$

The first term in r.h.s. of eq.(1) describes the spin motion in the presence of both static (*B*) and fluctuating ($h_{az}(t)$, $h_{bz}(t)$) magnetic fields. Here $\omega_o = \frac{1}{2}\mu_B B(g_a - g_b)$, $\omega(t) = \frac{1}{2}\mu_B\left(g_a h_{az}(t) - g_b h_{bz}(t)\right)$, $\hat{H}_o^x\rho = \left[\hat{S}_{az} + \hat{S}_{bz}, \rho\right]$.

The second term in r.h.s. of eq.(1) describes the fluctuations of the magnetic field that are characterized by the ω-space diffusion coefficient γ and the average fluctuation magnitude Δ.

The third term in r.h.s. of eq.(1) describes the first-order decay of the radical pair. We have considered the case of a simultaneous S and T recombination, both occurring at a rate constant κ.

To solve eq.(1), we have applied the following transformations:

$$\widetilde{L} = \exp\left(-\frac{i\Delta^2}{\gamma}\partial_\omega \hat{H}_o^x\right)\cdot\hat{L}\cdot\exp\left(\frac{i\Delta^2}{\gamma}\partial_\omega \hat{H}_o^x\right); \quad \widetilde{\rho} = \exp\left(-\frac{i\Delta^2}{\gamma}\partial_\omega \hat{H}^x\right)\cdot\rho. \qquad (2)$$

The transformed eq.(1) was expanded up to $O(\Delta/\gamma)$, and integrated over time. Thus, we have obtained a closed-form solution at $t=\infty$ in the fast fluctuation limit ($\Delta/\gamma < 1$).

For a radical pair in an initial T_o state, the probability of singlet recombination (P_S) is

$$P_S = \frac{\dfrac{2\Delta^2}{\gamma}\left(\kappa + \dfrac{4\Delta^2}{\gamma}\right) + 2\omega_o^2}{\left(\kappa + \dfrac{4\Delta^2}{\gamma}\right)^2 + 4\omega_o^2}. \qquad (3)$$

The value of P_S can be used to estimate the S-T_o conversion efficiency in presence of the fluctuating magnetic fields. If the efficiency of the S-T_o conversion is low, all radicals will recombine in T_o-state ($P_S = 0$). For a highly efficient S-T_o conversion, half of the radicals will recombine in S state and the other half will recombine in T_o-state ($P_S = 0.5$).

According to eq. (3), the effects of the magnetic field fluctuations appear only when the rate of the fluctuation change (γ) is comparable to (or smaller than) the other parameters of the system. The effects of the magnetic field fluctuations vanish if the fluctuations occur very quickly ($\Delta/\gamma << 1$).

Depending on the ratio of κ and ω_o, the fluctuating magnetic fields can either substantially increase or slightly decrease the S-T_o conversion efficiency (Fig.1). However, for high fluctuation magnitudes ($\Delta >> \omega_o$), the S-T_o conversion efficiency only increases with Δ (cf. Fig.1).

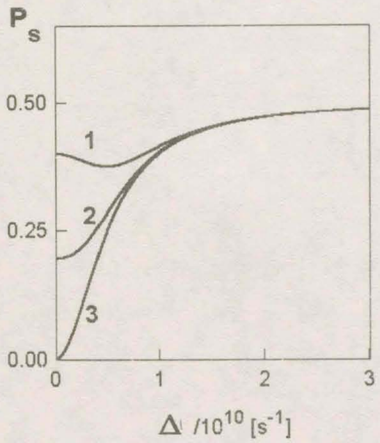

Fig.1. The singlet recombination probability (P_S) vs. the magnitude of the field fluctuations (Δ). The fluctuating magnetic fields are absent for $\Delta=0$.

Parameters: $\gamma = 10^{11}$ s^{-1}, $\kappa = 10^9$ s^{-1}.

Curve 1: $\omega_o = 10^9$ s^{-1}.

Curve 2: $\omega_o = 4*10^8$ s^{-1}.

Curve 3: $\omega_o = 0$.

Thus, the fluctuations of the magnetic field can indeed manifest in the radical pair recombination in the high magnetic fields. One can expect that similar effects can occur also in lower magnetic fields, where it is necessary to take into account the S-T_+ and S-T_- transitions. We are currently extending the model to study the low-field effects.

POSTER 19

LUMINESCENCE QUENCHING IN GEMINATE PAIRS.

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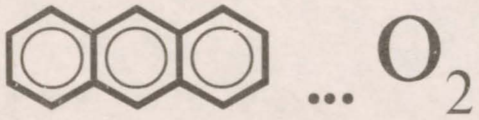
The geminate pair is primary product of many photochemical reactions. The further chemical transformations are controlled by reactivity and mobility of the partners. Most of developed techniques can measure only the chemical products and can not control the particle mobility. We developed the method that allows to get the information about particle mobility of the partners near each other.

The main idea is very simple. Geminate pair is prepared at the first stage by the photolysis of appropriate molecule followed by luminescence excitation one partner from pair. The other molecule quenches the luminescence. The quenching efficiency will depend on the distance between two partners and hence on their mobility.

This method is demonstrated on the geminate pair prepared by photolysis anthracene endoperoxide:



Oxygen is a quencher of anthracene luminescence. Quenching take place via exchange mechanism with a decrement near 1 A. This pair allow to study the oxygen mobility in a distance range 4 - 8 A between partners.

The luminescence pair quenching was studied in squalane and alcohol matrices at low temperatures near 77 K. Phenanthrene phosphorescence

quenching was studied in the same conditions what allow to increase the temperature range. The main results:

The mobility of molecular oxygen in squalane within the temperature range 100-155 K has been studied by phenanthrene phosphorescence quenching and in the range 77-105 K by anthracene luminescence quenching in geminate pairs. It has been demonstrated that both methods give the close results.

This method can be applied to the oxygen mobility studies in polymethylmetacrilate in a temperature range 77-110 K. Energy activation for diffusion process is equal 4 kkal/mole. The resultes demonstrate the wide distribution in diffusion coefficient values.

The approximation of continual diffusion has been shown to be adequate in describing most of the kinetic curves for both phosphorescence quenching and separation of geminate pairs.

It has been established that the slowing down of oxygen molecule mobility with time in alcohol matrices is directly related to the relaxation of alcohol matrices and is not caused by the local relaxation of matrix near luminescent molecules.

The method proposed for determining of the diffusion coefficient of oxygen by the separation of geminate pairs allows one to measure the values of mobility up to $D \sim 10^{-23}$ cm^2/s.

POSTER 20

CIDNP IN THE PHOTOLYSIS OF COENZYME B_{12} MODEL COMPOUNDS

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To date, the photolyses of coenzyme B_{12} and its analogs have received study by spin chemistry techniques (CIDEP and the influence of external magnetic field (MF) on the product yield). It is generally accepted that Co-C bond cleavage is a primary act of photolysis. The fact, that UV irradiation results in Co(III)-C bond breaking with the diffusion of alkyl radicals into the bulk and partial back recombination, may be considered of as conclusively established. However, the results of CIDEP and magnetic field effects experiments in the reaction under study have lead to controversial conclusions on the multiplicity of reactive state. For example, it follows from the sign of magnetic field effect (decrease in the yield of reaction product, Co(II) complex, as the applied MF is increased from geomagnetic one to 0.1 T) that Co(III)-C bond cleavage occurs from the singlet state [1]. On the other hand, analysis of CIDEP effects formed in the photolysis of methylaquacob(III)aloxime suggests the triplet primary radical pair [2]. This brings up the question: What is the multiplicity of the state where Co-C bond cleavage takes place?

This communication presents the results of application of one more spin chemistry method, ^{1}H CIDNP to study the photolysis of coenzyme B_{12} model compounds, ethylcob(III)-bis(salicylidene)ethylenediamine **EtCo(III)salen** and benzylaquacobaloxime **BzCo(III)(aq)(dmg)$_2$**, with the special aim to determine the multiplicity of reactive state.

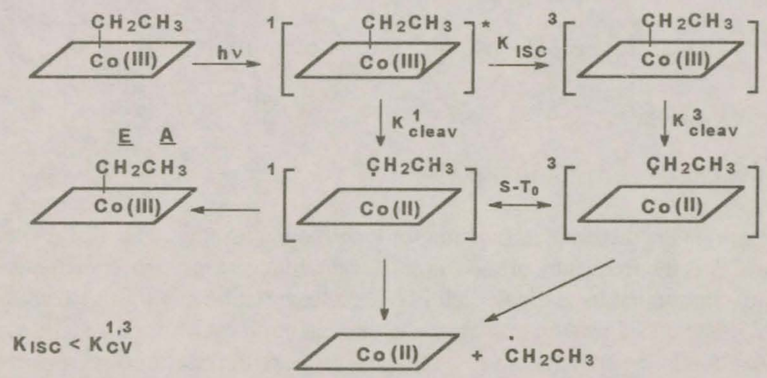
Note the important feature of the process: final reaction products are paramagnetic (Co(II) complexes), and this imposes essential restrictions upon the possibilities of CIDNP observations (line broadening of NMR signals as the reaction product is accumulated).

During the photolysis of EtCo(III)salen in CD_2Cl_2 the protons of the ethyl group of initial compound are polarized (emission, E, - CH_2; absorption, A, - CH_3). The observed polarization effects are most likely attributed to radical pair (RP) with ethyl radical with the following characteristics, Co(II)salen: g = 2.197, A(^{59}Co) = 8.82 mT; I(^{59}Co) = 7/2; Et$^{\bullet}$: g = 2.0025, A(CH_2) = -2.24 mT; A(CH_3) = +2.69 mT.

For the case of these unusual magnetic resonance parameters, it is necessary to note that in this RP the product $\omega_{S-T_0} \times \tau >> 1$ (here, the frequency of S-T_0 transitions $\omega_{S-T_0} = \Delta g H_0$; and H_0, the magnetic field strength of the employed NMR spectrometer, equals to 2.14 T). In the frames of RP theory this corresponds to the case of so-called “long-lived” radical pairs. Under these circumstances, the exact calculations are necessary for consideration of CIDNP intensities in S- and T-pairs. We have performed the calculations for the ethyl protons of initial EtCo(III)salen, the product of Co(II)salen recombination with ethyl radical. Calculated data show that the observed CIDNP signs correspond to *singlet* multiplicity of the RP. Thus, the experimentally observed CIDNP sign corresponds to the preferred homolysis of Co-C bond in the singlet excited state of the complex. It should be recollected that similar conclusion has been drawn on the basis of analysis of magnetic field influence on the photolysis of B_{12} model compounds. Taking into account significant variation between CIDEP enhancement coefficients for the effects formed via RP and triplet mechanisms, one may reason that even slight fraction of the radicals demonstrating CIDEP formed by triplet mechanism could be totally responsible for the observed electron polarization. At the same time, MF influence and CIDNP effects would correspond to the main reaction pathway, namely, to the decomposition from the singlet state.

All above reasoning has allowed us to propose the following scheme of the process under study (Scheme 1).

SCHEME 1



Financial support of Russian Foundation for Basic Research (Grant No. 94-08976) is gratefully acknowledged.

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POSTER 20

CIDNP IN THE PHOTOLYSIS OF COENZYME B_{12} MODEL COMPOUNDS

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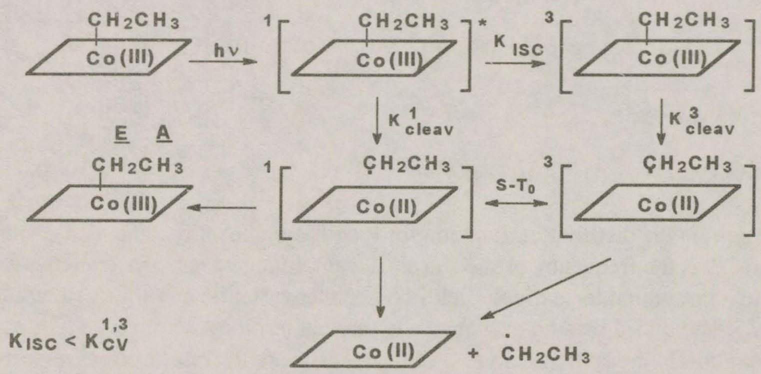
Note the important feature of the process: final reaction products are paramagnetic (Co(II) complexes), and this imposes essential restrictions upon the possibilities of CIDNP observations (line broadening of NMR signals as the reaction product is accumulated).

During the photolysis of EtCo(III)salen in CD_2Cl_2 the protons of the ethyl group of initial compound are polarized (emission, E, - CH_2; absorption, A, - CH_3). The observed polarization effects are most likely attributed to radical pair (RP) with ethyl radical with the following characteristics, Co(II)salen: g = 2.197, A(^{59}Co) = 8.82 mT; I(^{59}Co) = 7/2; Et$^{\bullet}$: g = 2.0025, A(CH_2) = -2.24 mT; A(CH_3) = +2.69 mT.

For the case of these unusual magnetic resonance parameters, it is necessary to note that in this RP the product $\omega_{S-T_0} \times \tau >> 1$ (here, the frequency of S-T$_0$ transitions $\omega_{S-T_0} = \Delta g H_0$; and H_0, the magnetic field strength of the employed NMR spectrometer, equals to 2.14 T). In the frames of RP theory this corresponds to the case of so-called "long-lived" radical pairs. Under these circumstances, the exact calculations are necessary for consideration of CIDNP intensities in S- and T-pairs. We have performed the calculations for the ethyl protons of initial EtCo(III)salen, the product of Co(II)salen recombination with ethyl radical. Calculated data show that the observed CIDNP signs correspond to *singlet* multiplicity of the RP. Thus, the experimentally observed CIDNP sign corresponds to the preferred homolysis of Co-C bond in the singlet excited state of the complex. It should be recollected that similar conclusion has been drawn on the basis of analysis of magnetic field influence on the photolysis of B_{12} model compounds. Taking into account significant variation between CIDEP enhancement coefficients for the effects formed via RP and triplet mechanisms, one may reason that even slight fraction of the radicals demonstrating CIDEP formed by triplet mechanism could be totally responsible for the observed electron polarization. At the same time, MF influence and CIDNP effects would correspond to the main reaction pathway, namely, to the decomposition from the singlet state.

All above reasoning has allowed us to propose the following scheme of the process under study (Scheme 1).

SCHEME 1



Financial support of Russian Foundation for Basic Research (Grant No. 94-08976) is gratefully acknowledged.

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POSTER 21

KINETIC THEORY OF NMR SPECTRA FOR SOLIDS. TWO KINDS OF SPINS

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In this work, our analytical theory of NMR spectra for the substances containing one kind of spins [1] is extended to the case of two kinds of spins. Universality of the theory is determined by the generality of the elementary dynamic process of dipole precession in the external and neighborhood dipole local fields, which is in the basis of derivation of the kinetic equations.

The kinetic equations for macroscopic variables $\sigma^{\beta}(h, t)$, $\beta = x, y, z$, which are components of the dipole densities in the longitudinal local field h at the moment t, prove to be the most convenient. Hereinafter, we will term them simply " polarization of layer" and denote $\sigma^{\beta}(h, t) = \sigma^{\beta}$. These kinetic equations were obtained in [1] with regard to the dipole precession in local magnetic fields:

$$\partial\sigma^x/\partial t = -(\Delta + 3h/2)\sigma^y - (3/2 - \alpha)(-h\sigma^y + h\sigma_0^y + \sigma_1^y) + (\sigma_0^x - \sigma^y)/\tau_{\perp} - \sigma^x/T_{\perp}$$

$$\partial\sigma^y/\partial t = (\Delta + 3h/2)\sigma^x + (3/2 - \alpha)(-h\sigma^x + h\sigma_0^x + \sigma_1^x) + (\sigma_0^y - \sigma^y)/\tau_{\perp} - \omega_1\sigma^z - \sigma^y/T_{\perp}$$

$$\partial\sigma^z/\partial t = \omega_1\sigma^y + (\sigma_0^z + \sigma_1^z h/\langle h^2\rangle - \sigma^z)/\tau_{\parallel} + (\sigma_{eq}^z - \sigma^z)/T_{\parallel z} - \sigma_1^z h/\langle h^2\rangle T_{\parallel D}$$

$$\sigma_0 = \int\sigma(h,t)g(h)dh, \quad \sigma_1 = \int\sigma(h,t)hg(h)dh, \qquad (1)$$

where $g(h)$ is the distribution function for longitudinal local fields in dense spin systems, Δ is the frequency off-set, ω_1 is the amplitude of resonance alternative field, h is the longitudinal local dipole field, $1/\tau_{\perp}$ is the variation rate for the longitudinal local fields induced by spin exchange and thermal motion of atoms, $1/\tau_{||}$ is the rate of equilibration in the spin system of a solid, $1/T_{\perp, //}$ are the rates of transverse and longitudinal relaxation, respectively. The relaxations are coupled by thermal motion, which leads to the absorption of a quantum at a Larmore frequency ω_0. $T_{//z}$, $T_{\|D}$ are the times of longitudinal spin-lattice relaxation of the Zeeman and dipole--dipole reservoirs. In deriving (1), the Hamiltonian of the dipole--dipole interaction (DDI) was written in the form: $H_d^z = \Sigma\, b_{ik}(3S_i^zS_k^z\ S_iS_k) \equiv 3H_{zz} - H_{is,}$ where $H_{is} = H_{xx} + H_{yy} + H_{zz}$; b_{ik} are the known coefficients of DDI .

The contribution from $3H_{zz}$ is defined by terms $3h\sigma^y/2$ and $3h\sigma^x/2$ in (1). For the contribution proportional to $(3/2 - \alpha)$ (which is the isotropic component of DDI H_{is} between the spins), the variation rates of layer polarization are determined by five physical parameters of a given interaction: inasmuch as the contribution is associated with the dipole precession in the local field, it must be proportional 1) to the local field h, and 2) to the layer polarization components $\sigma^{x,y}$; 3) the H_{zz} component of isotropic interaction makes an exactly calculated contribution proportional to $h\sigma^{x,y}$ to the rate of variation of layer polarization. Since the interaction H_{is} describes the spin-spin polarization exchange, its contribution goes to zero 4) at multiplying by the function $g(h)$ and at integrating over all the layers, and 5) in case of equal polarization of the layers. It should be noticed that, for the case $\omega_1 = 0$, these kinetic equations were derived previously from the equation of density matrix using a method of memory functions [2].

The suggested method makes it possible to derive kinetic equations and, therefore, to calculate the observed NMR and ESR spectra and to define the unknown parameters of different spin systems.

In this work, we studied a system with two kinds of nuclei: I-nuclei (those affected by the resonance field) and S-nuclei (those affected by the nonresonance field).

In the experiments [3], the absorption line of S-nuclei was observed depending on the resonance-field amplitude affecting I-nuclei. For the description of the data points in the system containing two kinds of spins, one can simply add the longitudinal local field $h_{IS} = h\cos\Omega t$ $(\Omega = -\gamma H$, H is the amplitude of the resonance RF field, γ is the hyromagnetic ratio for I-nuclei) induced by stirred spins to (1). It is important that this field together with the field h_{SS} leads not only to broadening the observed absorption lines, but also to an additional phase shift and disorder in orientation of S-spins. This disorder results in disappearance of the isotropic part of H of the exchange interaction among the polarization of the layers in (1), which makes it possible to solve the problem only in longitudinal local fields. From system (1), we derived the kinetic equation for the S-spin polarization of layer. For the purpose, we introduced new variables:

$$F(h,t) = \sigma^x(h,t) + i\sigma^y(h,t), \qquad F_0(t) = \int g(h)F(h,t)dh, \qquad (2)$$

At $\alpha = 3/2$ and (2), we have

$$dF/dt = I(3h_{SS}/2 + h_{IS})F + (F_0 - F)/\tau_{\perp} - F/T_{\perp}, \qquad (3)$$

where h_{SS} is the local field of the homonuclear interaction, h_{IS} is the local field of heteronuclear interaction. Upon introducing new variables:

$$F = \exp(-ih_{IS}\int\cos\Omega\tau d\tau)\, F = \exp(-ih_{IS}(\sin\Omega t)/\Omega) \qquad (4)$$

the kinetic equation (3) has the form

$$dF/dt = i3h_{SS}F/2 + (F_0 - F)/\tau_{\perp} - F/T_{\perp}, \qquad (5)$$

that is, we obtained the well-known equation [2] for the polarizations of the layer.

Computer simulation of (5) with due regard of (4) provides a solution which agree well with the experimental results for polycrystalline NaF [3], where the absorption line on the Na nuclei was observed upon the action of resonance field on F nuclei.

This work was supported by the Russian Foundation of Basic Research.

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POSTER 22

MAGNETIC FIELD EFFECTS ARE THE INSTRUMENT FOR RECORDING THE "OBSERVATION THRESHOLD" OF SOLVATED RADICAL-IONS IN POLAR MEDIA DURING ELECTRON PHOTOTRANSFER REACTIONS.

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Although the mechanism of electron reactions involving electron phototransfer (EPTR) has been studied for many years, there are a lot of unclear questions of principle importance. Particularly, these are the questions of the detection (or establishment) of the instant at which the solvated radical-ions (SSIP) arise in media with the low values of constant dielectric medium permeability ε with its value being varied. The present contribution proposes one more method to extract information necessary for solving the problem. This method is that of magnetic field effect observation (MFEM) in the recombination products of radical pairs depending on the ε value.

The essence of MFEM is in the fact that the effect of applied external magnetic field (B) on the yield of the recombination products of solvated radical-ions can be recorded only if the pair partners are separated by distance r_o at which the value of exchange integral $2J(r_o)$ of recombining radicals becomes comparable to or less than the values of the effective hyperfine interaction constant (A_{eff}) of these radicals.

The r_o value is usually 1 nm [1] which is quite sufficient for the formation of the "coat" of solvent molecules around the radical-ion. However, the more important moment is a thermodynamic possibility of SSIP formation, i.e. a principle possibility for radical-ions to part. Thus, the correlation between the MFE "observation threshold" and thermodynamic possibility of SSIP formation could be expected.

To demonstrate this situation we have measured the MFE magnitude in electron phototransfer for the system pyrene+N,N-dimethylaniline, pyrene +N,N-diethylaniline and pyrene+para-dicyanobenzol in the recombination products of triplet radical-ion pairs depending on ε.

MFE was measured from the intensity of the delayed fluorescence of pyrene (I^{df}) excimers at λ=475 nm. The excimers form in EPTR due to the T-T annihilation of pyrene molecules [2]. The DF intensity was measured 300 ns after system photoexcitation. The MFE magnitude is of the form:

$$\kappa = I^{df}(300G)/I^{df}(0) \qquad (1)$$

where $I^{df}(300G)$ and $I^{df}(0)$are the intensities of delayed excimer fluorescence with and without B.

Figures Ia and b depict the dependencies of MFE magnitude for the systems Py+DMA and Py+DCB. For the system Py+DEA the dependence of κ on ε (within experimental error ±3%) is similar to that for the system Py+DMA. Figure 2 shows the dependence of the changes in the free energy ΔG of the exciplex formation (a) of solvated radical-ions (b) and solvation-separated RIP (d) on ε for the system Py+DMA [3]. The similar

dependencies hold for the system Py+DEA [4]. For the system Py+DCB the dependence of the change in the G value for solvated radical-ions coincides with that for the system Py+DEA [5] and for exciplexes it is given in Fig. 2c.

Comparing the data in Figs. 1 and 2 it is seen that the MFE "observation thershold" correlates, as viewed from the low ε values, with a thermodynamic possibility of radical-ion formation which testifies to the possibility to use MFEM for studying the mechanism in EPTR.

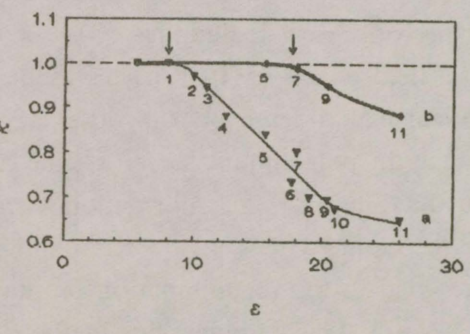

Fig. 1. The dependence of magnetic field effect κ on the ε value. a - for the system Py (10^{-4}M) + p-DCB ($2{*}10^{-2}$M); b - for the system Py (10^{-4}M) + DMA ($2{*}10^{-2}$M). 1-1-decanol; 2-octanol: 3-heptanol; 4-hexanol; 5-amyl alcohol; 6-1-butanol; 7-isobutanol; 8-isopropanol; 9-n-propanol; 10-allyl alcohol; 11-ethanol.

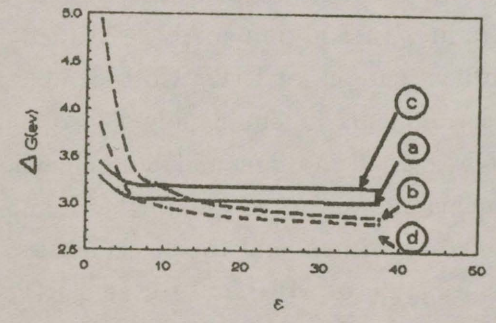

Fig. 2. The dependence of the change in the free energy ΔG of the formation of exciplexes (a), solvated SSIP (b) for the system Py+DMA (a) and exciplexes for Py+p-DCB (c) on the dielectric medium constant ε.

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POSTER 23

MAGNETIC FIELD EFFECTS AND THE MECHANISM OF CHEMICAL REACTIONS WITH ELECTRON TRANSFER.

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Although there is a great number of papers studying the mechanism of reactions involving electron phototransfer (REPT), this problem is still open to argument and can be solved using only new techniques. One of these techniques is the method of magnetic field effects (MFE). The present contribution reports the data of numerical experiments on the observation of MFE in REPT recombination products in polar liquid solvents. The application of this method seems quite justified because the information extracted is often unavailable for conventional techniques.

Magnetic field effects were recorded in the recombination products of singlet and triplet radical-ion pairs (RIP) by luminescent method with nanosecond time-resolution. The experiments were made in medium of different polarity, viscosity and temperature. In addition to it was varied the composition of solution and the partners nature of RIPs. Considerable attention has been given to MFE measurements in liquid polymer solutions and systems with RIP accepters. It was used constant and pulse magnetic field. The "magnetospectral" experiments allowed us to obtain the unknown information: a) to reveal the existence of excimers and triplet exciplexes; b) to establish correlation between the formation of MFE and solvated RIP; c) to verify the phenomenon of microheterogeneity in binary solutions; d) the RIP life time and so on.

POSTER 24

THE EFFECT OF THE MODULATION OF THE EXCHANGE INTEGRAL ON THE TIME-RESOLVED ADMR SPECTRUM IN THE FOLYMETHYLENE LINKED SYSTEM OF XANTHONE AND XANTHENE.

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Hisao Murai, Tohru Azumi.
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We applied the time-resolved RYDMR on the polymethylene linked xanthone and xanthene by monitoring the transient absorption (hereafter we call this technique time-resolved ADMR) of the intermediate biradical generated from an intramolecular hydrogen abstraction reaction in the polymethylene linked system of xanthone and xanthene. The time resolved spectra are shown in figure 1. The important feature of the spectra are as follows.

1. Spectrum is composed of the positive component (component I) at around 350 mT and the negative component (component II) whose bandwidth is very large(300 ~ 380 mT). The positive effect shows the deceleration of S-T conversion due to the spin locking effect and the negative one shows the acceleration of the inter system crossing by the pumping of the population.
2. Spectral bandwidth of the negative component is too large to be explained by the hyperfine structure of the terminal radicals (hydroxanthyl and xanthyl radical) or the broadening by the microwave power (B_1~3 mT).
3. The positive component appears within 200 ns after laser irradiation. In contrast, the negative component appears later than 200 ns.

We discuss the effect of the modulation of the exchange integral on the spin dynamics of the radical pair by the spectral features of the time-resolved ADMR spectra. For this purpose, we theoretically calculate the time-resolved ADMR spectra by the two site model. The model for the calculation is shown in figure 2. The results of the calculation are shown in figure 3. Figure 3a shows the calculated spectra without the modulation of the exchange integral (constant J model). These spectra does not agree with the spectral feature of the observed spectra. We also calculate the spectra with the modulation of the exchange integral (modulated J model). In the calculation, we choose the parameters $J(1)$ and $J(2)$ so as to conserve the average value of the exchange integral (J_{av}). The result of the calculation is shown in figure 3b, and the spectral feature is similar with the observed one. Therefore, we conclude that the effect of the modulation of the exchange integral is very important for the time-resolved ADMR spectra. However, the total bandwidth of the observed spectra is much larger than that of the calculation, and we are now progressing the improvement of the model for the calculation.

We assign the component I as the spin locking effect due to the coupling between the triplet sublevels (we call it T-line), and the component II as the transition from the T_+ or T_- state to the S state which slightly mixes with the T_0 state (we call it S-line). The exchange integral shifts the S-line to the low and high magnetic field from the central part (T-line) of the spectrum, and the modulation of it causes the broadening of the spectrum by the dephasing between the singlet (S) state and the triplet states (T_+ and T_-). The existence and the broadening of the S-line is theoretically predicted by

Shushin et al[1] by the reduction of the two site model into the single site model. The line shape and the time dependence of the S-line strongly reflect the modulation of the exchange integral. Therefore we can discuss the detail of the feature of the modulation of the exchange integral by the analysis of the time-resolved ADMR spectra.

Ref. [1] A.I. Shushin; *Chem. Phys. Lett.* **1991,** *181*, 274.

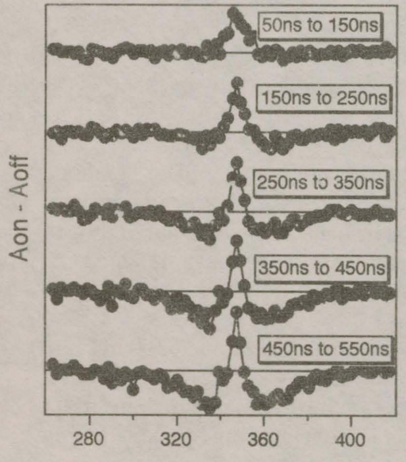
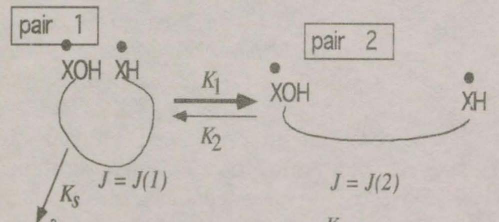


Figure 1

Two-site model



$$\frac{\partial\rho}{\partial t} = iL\rho = -i[\hat{H},\rho] - \hat{W}\rho - \hat{\Gamma}\rho - \frac{K_S}{2}[|S\rangle\langle S|,\rho]_+$$

$K_S = 6\times10^8 s^{-1}$ $K_2 = 1\times10^8 s^{-1}$ $K_1 = 70K_2$ $B_1 = 3$ mT

ref. (1)Y.Tanimoto,et al.;*J.Phys.Chem.* **1992,** 96, 9844.
(2)Y.Tanimoto,et al.;*Chem.Phys.Lett.* **1992,** 5, 188.

$\hat{\Gamma}$:Red-field matrix B_{loc}= 1.3 mT local magnetic field.
τ_c= 10ps correlation time.

Figure 2

Model 1 (Figure 1) constant *J* model

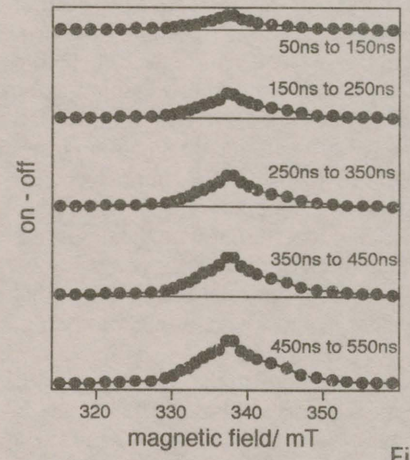
$$J(1) = J(2) = -0.81 \text{ mT}$$

Model 2 (Figure 2) modulated *J* model

$$J(1) = -5.68 \text{ mT} \quad J(2) = 0 \text{ mT}$$

$$J_{av} = \frac{K_2 J(1) + K_1 J(2)}{K_1 + K_2} = -0.81 \text{ mT}$$

a)



b)

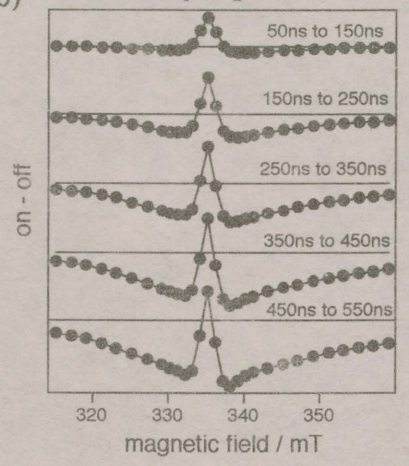


Figure 3

POSTER 26

GENERALIZATION OF THE RP EXPONENTIAL MODEL FOR THE INVESTIGATION OF THE ANISOTROPIC INTERACTIONS ROLE IN THE CIDEP AND CIDNP EFFECTS FORMATION

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Spin chemistry methods, such as, for example, CIDNP and CIDEP, are widely used in studies of the mechanisms of chemical reactions proceeding with the formation of radical pairs (RPs). The theory necessary for the interpretation of experimental evidence is well developed for the case where a chemical reaction proceeds in the liquid phase. It is assumed that anisotropic magnetic interactions for each radical of a pair are averaged by rapid rotation of particles, while anisotropic interparticle interactions are averaged in the course of the relative diffusion motion of partners. As a result, the Hamiltonian or Liouvillian describing spin dynamics in a pair are reduced to a sum of isotropic interactions: electron Zeeman interaction, interradical exchange and electron-nuclear hyperfine (hfi) ones. In this case, the approach using the Green functions makes it possible to divide the problem into two independent ones: the first problem - for spin degrees of freedom, and the second one - for classical degrees of freedom describing the relative motion of radicals [1].

Considerable recent attention has been focused on the systems which cannot be described adequately in the framework of the concepts developed for the description of reactions in nonviscous liquids. These are micelles, plastic crystals, molecular clusters in the gas phase, etc. This also refers to RPs with large constants and anisotropy (~1000 Oe) of hfi. In connection with this, of some interest is the development of such model of RP which, on the one hand, could correctly allow for anisotropic interactions, and, on the other hand, could admit simple solutions. We believe it reasonable to use exponential models (simple or two-position ones) as a basic. The experience shows that, most commonly, the application of the exponential model and its generalizations makes it possible to analyze qualitatively the influence of one or another parameter of the problem on spin polarization effects [2].

As an example, consider two-position model [3]. Let $\varphi_1(\vec{\Omega})$ and $\varphi_2(\vec{\Omega})$ be the probabilities to find RP in the first and second zones, respectively. These probabilities obey the set of equations

$$\frac{\partial}{\partial t}\varphi_1(\vec{\Omega}) = -\frac{1}{\tau}\varphi_1(\vec{\Omega}) + \frac{n}{\tau_c}\varphi_2(\vec{\Omega})$$

$$\frac{\partial}{\partial t}\varphi_2(\vec{\Omega}) = -\frac{n+1}{\tau_c}\varphi_2(\vec{\Omega}) + \frac{1}{\tau}\varphi_1(\vec{\Omega}) - \frac{1}{\tau_R}\left\{\varphi_2(\vec{\Omega}) - \int f(\vec{\Omega},\vec{\Omega}')\varphi_2(\vec{\Omega}')d\vec{\Omega}'\right\}$$

τ is the time of transition from the first zone to the second one, τ_c is the RP life time, n is the mean number of re-contacts, τ_R is rotational reorientation time (it is supposed that

Shushin et al[1] by the reduction of the two site model into the single site model. The line shape and the time dependence of the S-line strongly reflect the modulation of the exchange integral. Therefore we can discuss the detail of the feature of the modulation of the exchange integral by the analysis of the time-resolved ADMR spectra.

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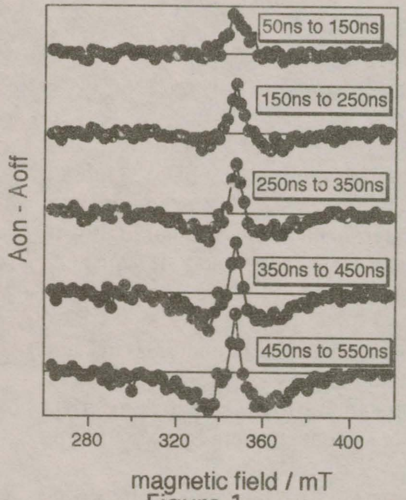
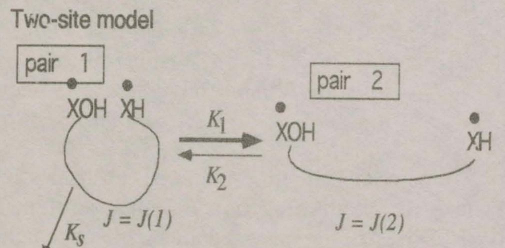


Figure 1



$$\frac{\partial\rho}{\partial t} = iL\rho = -i\left[\hat{H},\rho\right] - \hat{W}\rho - \hat{\Gamma}\rho - \frac{K_S}{2}\left[|S\rangle\langle S|,\rho\right]_+$$

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a)

b)

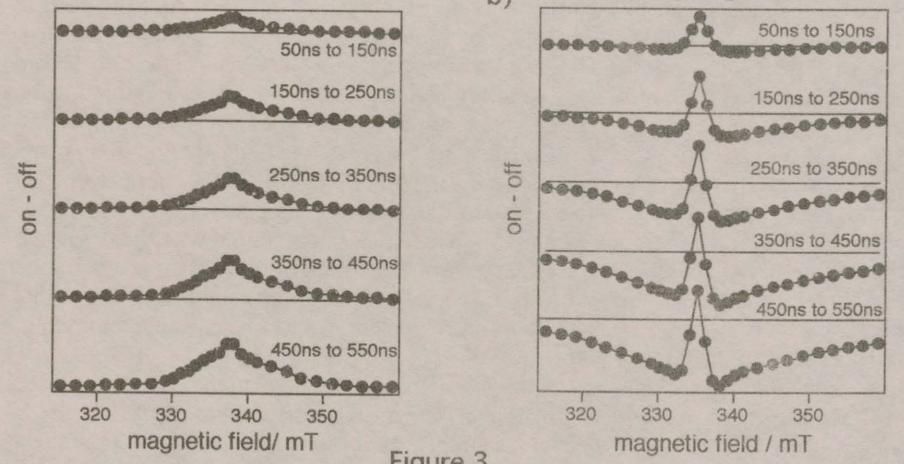

Figure 3

POSTER 25

TIME-RESOLVED CIDNP STUDY OF THE PHOTOREDUCTION OF KETONES BY TRIETHYLAMINE

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The photoreactions of acetone and benzophenone (BP) with triethylamine (TEA) in acetonitrile have been investigated by time-resolved CIDNP. The multiplet and net effects for educts and products have been first found. The influence of concentration of TEA as a chemical quencher and laser light (308nm) intensity on the CIDNP pattern and product yields has been observed.

For the reaction of TEA with BP with the variation of amine concen- tration the change of reactivities for singlet and triplet states of acetone has been achieved. At high light intensities two-photon process for alfa-cleavage of triplet acetone occurs.

Multiplet effect (A/E-type) CIDNP was observed for CH_2 and CH_3 protons of TEA, and also for CH_3CHN protons of coupling product during the photoreduction of BP by TEA.

From the analysis of CIDNP data it was concluded that for both cases the polarization is created mainly in neutral radical pair $COH...CH_3CHN(CH_2CH_3)_2$ with triplet electronic state. However, contrary to BP/TEA system the disproportion of ketyl and aminoalkyl radicals in acetone/TEA system is predominated. The more capacity of Ph_2COH radical to the recombination reaction rather than disproportion due to its resonance stabilizing feature.

This study once more allows to test a generalized radical-pair mechanism for the dehydrogenization of TEA by electron acceptors early suggested by us /Sh.A.Markarian, Zhurn.Org.Khimii (Russian J.Org.Chem.) 1982, v.18, p.252/.

POSTER 26

GENERALIZATION OF THE RP EXPONENTIAL MODEL FOR THE INVESTIGATION OF THE ANISOTROPIC INTERACTIONS ROLE IN THE CIDEP AND CIDNP EFFECTS FORMATION

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Spin chemistry methods, such as, for example, CIDNP and CIDEP, are widely used in studies of the mechanisms of chemical reactions proceeding with the formation of radical pairs (RPs). The theory necessary for the interpretation of experimental evidence is well developed for the case where a chemical reaction proceeds in the liquid phase. It is assumed that anisotropic magnetic interactions for each radical of a pair are averaged by rapid rotation of particles, while anisotropic interparticle interactions are averaged in the course of the relative diffusion motion of partners. As a result, the Hamiltonian or Liouvillian describing spin dynamics in a pair are reduced to a sum of isotropic interactions: electron Zeeman interaction, interradical exchange and electron-nuclear hyperfine (hfi) ones. In this case, the approach using the Green functions makes it possible to divide the problem into two independent ones: the first problem - for spin degrees of freedom, and the second one - for classical degrees of freedom describing the relative motion of radicals [1].

Considerable recent attention has been focused on the systems which cannot be described adequately in the framework of the concepts developed for the description of reactions in nonviscous liquids. These are micelles, plastic crystals, molecular clusters in the gas phase, etc. This also refers to RPs with large constants and anisotropy (~1000 Oe) of hfi. In connection with this, of some interest is the development of such model of RP which, on the one hand, could correctly allow for anisotropic interactions, and, on the other hand, could admit simple solutions. We believe it reasonable to use exponential models (simple or two-position ones) as a basic. The experience shows that, most commonly, the application of the exponential model and its generalizations makes it possible to analyze qualitatively the influence of one or another parameter of the problem on spin polarization effects [2].

As an example, consider two-position model [3]. Let $\varphi_1(\vec{\Omega})$ and $\varphi_2(\vec{\Omega})$ be the probabilities to find RP in the first and second zones, respectively. These probabilities obey the set of equations

$$\frac{\partial}{\partial t}\varphi_1(\vec{\Omega}) = -\frac{1}{\tau}\varphi_1(\vec{\Omega}) + \frac{n}{\tau_c}\varphi_2(\vec{\Omega})$$

$$\frac{\partial}{\partial t}\varphi_2(\vec{\Omega}) = -\frac{n+1}{\tau_c}\varphi_2(\vec{\Omega}) + \frac{1}{\tau}\varphi_1(\vec{\Omega}) - \frac{1}{\tau_R}\left\{\varphi_2(\vec{\Omega}) - \int f(\vec{\Omega},\vec{\Omega}')\varphi_2(\vec{\Omega}')d\vec{\Omega}'\right\}$$

τ is the time of transition from the first zone to the second one, τ_c is the RP life time, n is the mean number of re-contacts, τ_R is rotational reorientation time (it is supposed that rotation proceeds in the second zone only), $f(\vec{\Omega},\vec{\Omega}')$ is the density of the conditional probability that, as a result of one jump, orientation will be characterized by the angles $\vec{\Omega}$, provided that it was $\vec{\Omega}'$ before the jump (in particular, for uncorrelated rotation $f(\vec{\Omega},\vec{\Omega}') = \text{const}$).

In the presence of the Liouvillian of magnetic interactions, system (1) is easily generalized by introducing the corresponding density matrix and the Liouvillian of these interactions instead of the probability. For uncorrelated rotational motion, in some cases, the CIDNP and CIDEP effects can be represented by analytical formulae.

In the present contribution we have analyzed the influence of dipole-dipole interaction on CIDNP effects. It is shown that this influence can often be considerable, and decrease the observed effect essentially. The role of dipole-dipole interaction in the CIDEP effect formation has been studied, and its significance has been noted. Dipole-dipole interaction is of particular importance in considering the kinetics of magnetospin effects. In the framework of the models considered, the role of hfi anisotropy in the CIDNP formation has been studied, and the transition from "dynamic" regime of the influence to relaxation one has been analyzed.

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POSTER 27

INVESTIGATION OF THE PHOTO-FRIES REARRANGEMENT OF 1- AND 2-NAPHTHYL ACETATE.

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Typical photo-Fries rearrangement reactions [1] of 1- and 2-naphthyl acetate (1-NA and 2-NA) were investigated. The kinetics of these reactions were studied in detail by different experimental methods.

Stationary photolysis was used to determine the quantum yields of the reactions and the product distribution. The transient absorption spectra and kinetics were obtained by laser flash-photolysis. Two types of intermediates were observed during the reaction: a) naphthyl acetate triplet state (absorption maximum at 410 nm, second order decay is significantly accelerated by the piperylene as a triplet quencher) and b) naphthoxyl radical (absorption at 340-390 nm, its kinetics is insensitive to piperylene at concentrations up to 0.02 M).

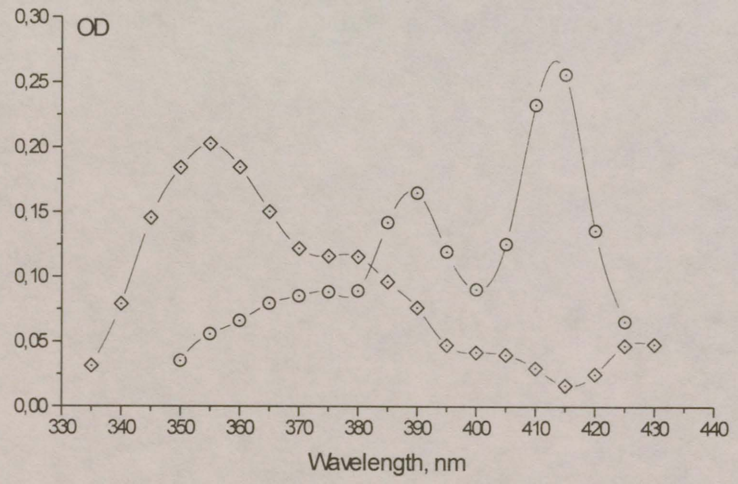
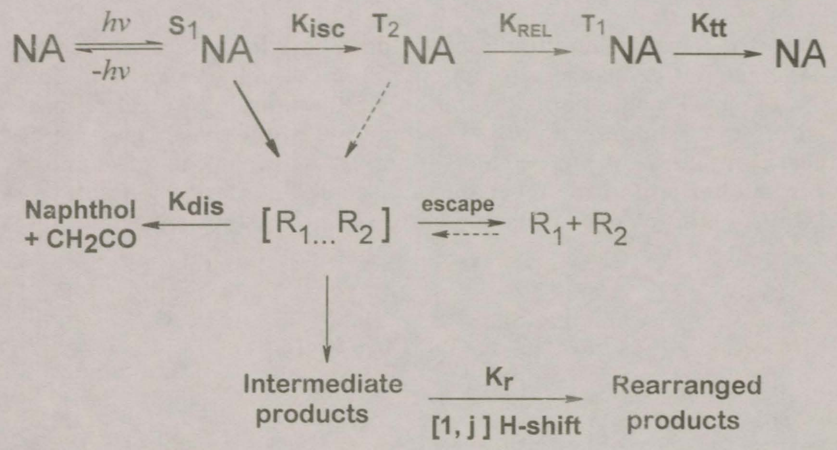


Figure 1. Transient absorption spectra of triplet 2-NA (circles) and of 2-naphthoxyl radicals (diamonds) in CH_3CN.

Time-resolved and steady-state studies of CIDNP effects in these reactions were carried out. The signs of the CIDNP of the main reaction products point to the triplet precursors of the radical pairs for 1-NA [2], while for 2-NA to the singlet ones. The influence of piperylene on the CIDNP sign and amplitude was investigated.

It is shown that the addition of piperylene has different effect on the product quantum yield, triplet state decay and CIDNP formation. The slope of the Stern-Volmer plot for the product quantum yield in the presence of piperylene is 4-8 M^{-1} [2] for 1-NA and 2 M^{-1} for 2-NA. For CIDNP intensity, the corresponding value varies within 75-300 M^{-1} for 1-NA [2] in different solvents and is about 60 M^{-1} for 2-NA in methanol. At the same time, even small amounts of piperylene (about 10^{-4} M) noticeably accelerate the triplet decay; the triplet quenching experiments yielded the triplet lifetime (in absence of any quenchers and T-T annihilation) of 5 μs.

These results allow us to suggest the following reaction scheme for 1-NA and 2-NA photolysis:



1. Light radiation excites the NA parent molecule into the first excited singlet state, which can either dissociate to yield a radical pair or transfer to the upper triplet state T_2. The singlet excited state is the main channel of product formation, but it makes a small contribution to the CIDNP.
2. Most of the T_2 triplet molecules relax to the T_1 triplet state; however, some of them dissociate yielding the same radical pair as that for the singlet precursor. This channel is of less importance, but it is responsible for the observed CIDNP effects.
3. The T_1 triplet state of naphthyl acetate is nonreactive, the main channel of its decay being the triplet-triplet annihilation.
4. The in-cage recombination of radical pairs competes with the fast disproportionation and escape; the formation of ketene observed in the CIDNP spectra is more pronounced for 2-NA.

Acknowledgments.
This work was supported by grants of Russian Foundation for Basic Research (Projects No. 96-03-32930 and No. 96-03-33982).

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POSTER 28

Influence of exchange interaction of radical ions on amplitude of recombination luminescence beats.

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Kinetics of recombination luminescence beats is calculated analytically in terms of a step-wise model of exchange interaction J(r) in radical ion pair. We considered the case of strong external magnetic fields and only ST_0-transions were taken into account. The obtained effect of suppression of beat amplitude is due to a dispersion of residence time of radical pairs inside strong exchange interaction zone. This mechanism of beat suppression is an alternate to the mechanism discussed earlier by Burshtein and Morozov [1]. In the limit of high polar medium we obtained an explicit formula for beat amplitude A:

$$A=\left|\left\{(r_0-R)+\left(\frac{R-b}{2}\right)\left[1+e^{-\sqrt{2}z\left(\frac{r_0-R}{R-b}\right)}\right]\chi(z)\right\}/\left[(r_0-b)\psi(z)\right]\right| \qquad (1)$$

$$\chi(z)=\frac{sh(z)}{z}\left(ch(z)+\frac{sh(z)}{\sqrt{2}}\right)^{-1}, \quad \psi(z)=ch(z)+\frac{sh(z)}{\sqrt{2}}, \quad z=\sqrt{\frac{i\delta}{D}}(R-b),$$

where r_0 is the initial distance in radical ion pair, b is the radius of recombination, R is a size of strong exchange interaction zone, δ is the frequency of ST_0-transitions, D is the relative diffusion coefficient of radical ions.
The size of strong exchange interaction zone is determined with the equation: J(R)=δ.

It is shown that the more strong electrostatic attraction of radical ions the more the amplitude of beats. Thus the above formula for A is a lower estimate of beat amplitude at the given parameters of exchange interaction. It is demonstrated how to redefine parameters of equation (1) to take into account an arbitrary value of Coulomb interaction of radical ions.

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POSTER 29

CIDNP Effects in Geminate Evolution of Consecutive Biradicals

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CIDNP effects observed in radical reactions in solution, where one of the members of a radical pair (RP) undergoes a chemical transformation, were a subject of many investigations. Of particular interest is the case where chemical transformations occur in a radical pair whose radical centers are linked by a polymethylene chain, i.e. in a biradical.

In this work, we report on a CIDNP effects arising in the photolysis of the α-substituted cyclic aliphatic ketones: 2,2,12,12-tetramethylcyclododecanone, 2-hydroxy-2,12-dimethylcyclododecanone, and 2,12-dihydroxy-2,12-dimethylcyclododecanone. In 2,2,12,12-tetramethylcyclododecanone, the effects of nuclear polarization were studied by Turro and co-workers by stationary ^{1}H and ^{13}C high-field CIDNP [1]. In these ketones, photoinduced cleavage of the α-C-C bond results in the formation of alkyl-acyl biradicals. The latter are subject to decarbonylation, which, therefore, plays the role of the above mentioned chemical transformation. In this case, the reaction can be described by the following scheme:

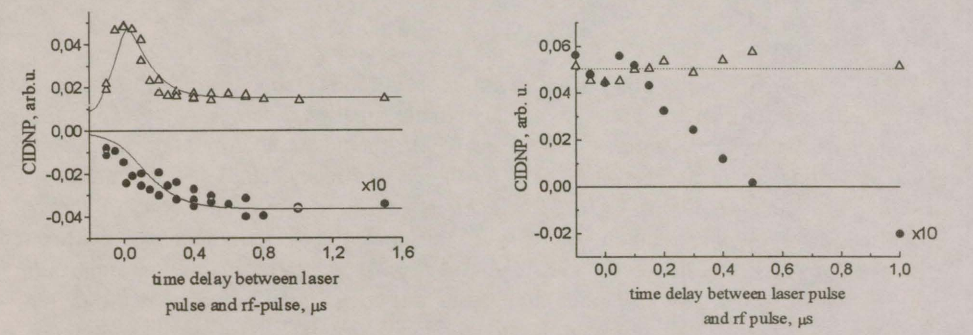
$$\begin{tikzcd}
K \arrow[r, "h\nu"] & {}^{T}K^{*} \arrow[r] & {}^{T}B_1 \arrow[r, shift left] \arrow[d, "-CO"'] & {}^{S}B_1 \arrow[l, shift left] \arrow[r] \arrow[d, "-CO"'] & Pr_1 \\
 & & {}^{T}B_2 \arrow[r, shift left] & {}^{S}B_2 \arrow[l, shift left] \arrow[r] & Pr_2
\end{tikzcd}$$

,

where Pr_1 and Pr_2 denote the sets of products of acyl-alkyl (B_1) and bis-alkyl (B_2) biradicals, respectively.

In the alkyl-acyl biradical, where Δg in nonzero, the net nuclear polarization is formed. By contrast, the bis-alkyl biradical arising from the decarbonylation exhibits no net CIDNP (Δg=0). At high magnetic fields, the signs of the nuclear polarizations for Pr_1 and Pr_2, as well as the CIDNP kinetics, depend on the decarbonylation rate. For the alkyl-acyl biradicals arising during the photolysis of 2,2,12,12-tetramethylcyclododecanone and 2-hydroxy-2,12-dimethylcyclododecanone, the decarbonylation is slow compared to the characteristic time of the geminate processes for the long-chain biradicals (tens of nanoseconds). In this case, biradical B_2 is formed in the nuclear spin states that have not reacted in primary biradical B_1. Thus, the products Pr_2 of the secondary biradical carry an escape type polarization, which is opposite in sign to the geminate one. For Pr_1, the CIDNP kinetics passes through a maximum and reaches a nonzero stationary value, which is determined partly by the decarbonylation rate. For Pr_2, the nuclear polarization increases monotonously in time and reaches a stationary value (Fig.1a).

The CIDNP memory effect [2,3] is expected in the case of "fast" decarbonylation, which occurs in 2,12-dihydroxy-2,12-dimethylcyclododecanone. This implies the same signs of the nuclear polarizations for Pr_1 and Pr_2 at short times. Under our experimental conditions, the CIDNP signals of Pr_1 are constant in time, while the nuclear polarization of Pr_2 decreases with time and changes its sign at relatively long times (Fig.1b). No net CIDNP arises in the bis-alkyl biradical with equal g-factors. The latter, however, provide the formation of a multiplet CIDNP.



a b

Fig.1. ^1H CIDNP kinetics for the recombination products of alkyl-acyl biradicals B_1 (Δ) and bis-alkyl biradicals B_2 (●) arising in the photolysis of 2,2,12,12-tetramethylcyclododecanone (a) and 2,12-dihydroxy-2,12-dimethylcyclododecanone (b).

A detailed analysis of CIDNP amplitudes allowed us to estimate the probability of the "hidden" back recombination of the biradicals to the initial ketone, as well as to determine the distribution of the products.

It should be noted that the decarbonylation reduces the biradical chain length and enhances the effective exchange interaction. At low magnetic fields the latter leads to different CIDNP field dependences for Pr_1 and Pr_2. Thus, CIDNP field dependences for Pr_1 and Pr_2 during the photolysis of 2,2,12,12-tetramethylcyclododecanone exhibit maxima at different magnetic fields. This fact indicates that the photolysis of the ketone under study involves two types of biradicals. The presence of consecutive biradicals was also confirmed by ^{13}C low- and high-field CIDNP.

Acknowledgements.

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POSTER 30

Time-Resolved CIDNP and Laser Flash Photolysis Investigation of the Kinetics and Mechanisms of Photoreactions of C_{60} with Triethylamine.

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Time-resolved CIDNP and laser flash photolysis were applied to investigate the electron transfer and the subsequent reactions during the irradiation of buckminsterfullerene in benzonitrile solution, containing triethylamine (TEA). It is known that photoexcitation of C_{60} produces the triplet within nanoseconds in high yield. It has a rather long lifetime ($\tau = 40$ μs), and under our experimental conditions decays exponentially. Addition of triethylamine to benzonitrile solution of fullerene shortens the triplet lifetime of C_{60}. The quenching rate constant estimated from the Stern-Volmer dependence is 6.3×10^8 $M^{-1}s^{-1}$. In our flash-photolysis experiments ($\lambda_{exc} = 308$ nm), the effective quenching rate constant is smaller than $k_q = 9.4\times10^8$ $M^{-1}s^{-1}$ reported in [1] ($\lambda_{exc} = 532$ nm) due to quenching of excited benzonitrile by TEA.

The CIDNP spectra obtained during the irradiation of C_{60} and TEA in benzonitrile exhibit the polarized signals of CH_2-protons of TEA. We have found that two types of radical pairs are responsible for CIDNP formation: $C_{60}^{\cdot -}$ $TEA^{\cdot +}$ and $TEA^{\cdot +}$ benzonitrile$^{\cdot -}$ (Fig. 1). The experiments carried out in the presence and in the absence of fullerene allowed us to separate the contribution to CIDNP originating from the radical ion pair $C_{60}^{\cdot -}TEA^{\cdot +}$.

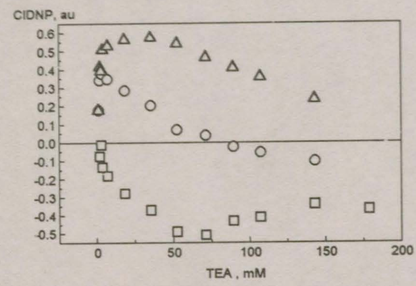

Fig. 1
Concentration dependence of CIDNP effects:
□ - TEA+benzonitrile
O - C_{60}+TEA+benzonitrile
Δ - C_{60}+TEA (difference)
$\tau = 0$, 60° rf-pulse (3 μs), 8 scans,
$[C_{60}] = 0.05$ mM

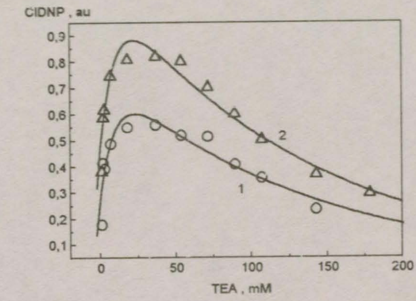

Fig. 2
Concentration dependence of CIDNP effects for C_{60}+TEA:
O - $[C_{60}] = 0.05$ mM
Δ - $[C_{60}] = 0.1$ mM
$\tau = 0$, 60° rf-pulse (3 μs), 8 scans

Absorptive CIDNP of CH_2-protons of $N(CH_2CH_3)_3$ unambiguously testified the formation of radical ion pairs:

$$^3C_{60} + TEA \xrightarrow{k_q} C_{60}^{\cdot -} + TEA^{\cdot +}.$$

CIDNP amplitude dependencies on TEA concentration for the radical pair $\overline{C_{60}^{\cdot-}TEA^{\cdot+}}$ are shown in Fig. 2. Initial growth of CIDNP amplitude is explained by the increase of the number of geminate radical pairs. Further increase of TEA concentration accelerates the degenerate electron transfer which results in the shortening of the lifetime of the geminate pairs. Thus the curves on Fig. 2 decay at a relatively high TEA concentrations.

Kinetic measurements showed that CIDNP amplitude grows monotonously in time and reaches stationary value. Initial rise of CIDNP corresponds to the formation of radical cation of TEA. The absence of the polarization decay can be explained by nuclear relaxation processes in $TEA^{\cdot+}$ radical cation and fast degenerate electron transfer ($k_e = 2.5 \times 10^9\ M^{-1}s^{-1}$ for TEA in acetonitrile [2]):

$$^*TEA^{\cdot+} + TEA \xrightarrow{k_e} {}^*TEA + TEA^{\cdot+}.$$

Acknowledgments

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POSTER 31

APPLICATION OF CIDNP METHOD FOR STUDYING THE ENERGY TRANSFER OF ELECTRON EXCITATION IN CONDENSED MEDIA

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In this work we have used the CIDNP method to study the radiationless energy transfer of electron excitation in photochemical decomposition of isotope-mixed molecules of aldehydes and ketones in the condensed phase. In this case, we were guided by the following considerations. The processes of energy transfer are commonly studied using the spectral and kinetic equipment of both the spectroscopy of electron paramagnetic resonance (EPR) and luminescence methods [1.2]. However, in many cases these techniques are limited by the application conditions (e.g. the ESR method can be applied to study energy transfer over intermediate radicals at low temperatures) or by the degree of information reliability (rigid requirements for luminescence methods because of the existence of chemical reaction channel), etc. When the CIDNP effects are studied in isotope-mixed molecules, the effects of nuclear spin polarization are observed that substantially differ from the effects for the molecules of one isotope and depend on the isotope composition of the solution. Computed analysis of experimental data in the frame of the model of CIDNP formation according to the S-To mechanism has showed that the dependences of CIDNP effects on the relation between the molecules of different isotope composition in solution resulted from the energy transfer of electron excitation from excited molecules of a heavy isotope to the molecules of a light isotope. Such a localization of energy leads to a selective photochemical decomposition of isotope-mixed molecules which is recorded by the CIDNP effects of photolysis products. The influence of intamolecular intersystem crossing rate on CIDNP formation has been investigated in the molecules with different isotopic composition.

Based on this, the mechanism of isotope-selective photochemical reactions was proposed. This mechanism will be effective enough if, first, the molecules of different isotope composition substantially differ in the energy of electron excitation, and second, the energy transfer is faster than excitation deactivation, i.e. both the relaxation of a molecule in the ground state and the photochemical decomposition of a molecule). Comparing the results obtained by observing the CIDNP effects for the molecules of different isotope composition, we have drawn the conclusion on the priority of the ways and mechanisms of the reactions under study. A theoretical analysis of experimental results has allowed us to study the mechanisms of the formation of nuclear polarization formation.

The parameters were obtained that characterize the processes of CIDNP formation and energy transfer in photochemical reactions.

ACKNOWLEDGEMENT. This work was supported by the Russian Foundation for Fundamental Researches (project 96-03-32956).

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POSTER 32

CIDNP IN ION - RADICAL REACTIONS IN THE GAS PHASE

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It is correctly reasoned that in the gas - phase radical reactions the cage effect to be absent at not very high densities - the fragments of decomposing molecule fly apart rapidly. Therefore, the attempts to find nuclear polarization in gas-phase reactions have not been undertaken for a long time.

However, for the special class of photochemical reactions the cage effect manifests itself in the gas phase as well. This is reactions of biradicals. The CIDNP effects in such reactions have been revealed and studied [1]. In these systems a complete divergence of radical centers is impossible and the recombinations occur almost with the unit probability.

There is another class of photochemical reactions where the cage effect can often be expected. There are the reactions involving ion-radicals. We have already briefly reported [2] on the observation of CIDNP in reactions of electron transfer in gas-phase oxidation of triethylamine by naphthalene. Acetonitrile has been used as a polar buffer gas.

In the photolysis of the liquid solutions of naphthalene and triethylamine in acetonitrile the greatest polarization is observed on triethylamine methylene protons. The spectra also exhibit the signal induced by polarization of naphthalene and diethylvinylamine molecules. The polarization sign in triethylamine and naphthalene is positive and in diethylvinilamine it is negative.

In the gas phase the signal intensity in dark NMR spectra varies with the temperature of gas mixture. The pattern of CIDNP effects differ in liquid and gas phase. First, the polarization coefficients depend on temperature, composition, and vapor pressure. As the gaseous mixture pressure increases the CIDNP intensity maximum shifts towards high temperature. Second, near 480 - 500 K the polarization sign of methylene protons changes from absorption to emission.

We believe that the photoinduced electron transfer from a triethylamine molecule to naphthalene with producing of ion-radical pair (IRP) is the principal primary photochemical act
both in the gas and liquid phases. IRP having a large dipole moment can be the center of condensation. The encounter of the molecules of polar buffer gas having their own dipole moment with
such "primary" pair will lead to their adsorption and increase of a microdroplet.

A direct proof that the observed CIDNP effect arises in the gas phase is the experiment with a small (1 μl) quantity of reaction mixture. A simple estimation shows that the quantities of any substance are insufficient for the formation of the condensed phase even at the lowest temperature within the range studied.

The estimate shows that the cluster contains near 5 - 6 acetonitrile molecules. The polar molecules of buffer gas are hardly capable of filling more than 1 - 2 coordination spheres around the "primary" IRP. The cluster being formed play the rule of a " age" for radical pairs residing in them. As the result of translational and rotational motion, the atoms carrying the spin density of radicals can change the relative position, with the exchange interaction between them being "switched off". The formation of "solvate - separated" pair also possible. In either case, there is a possibility of singlet - triplet transitions, and the CIDNP formation by ion-radical mechanism.

The observed CIDNP spectra depend on temperature, the total amount of the naphthalene - triethylamine - acetonitrile mixture, and the ratio of the components in it. We have failed to detect the CIDNP effects in the absence of buffer gas, as well as in the case where nonpolar gases - cyclohexane or pentane were used.

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POSTER 33

THE ROLE OF EXCITED STATES IN THE FORMATION OF CIDNP EFFECT IN PHOTODISSOCIATION OF ALDEHYDES AND KETONES IN CONDENSED MEDIA

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In [1,2] we have reported on CIDNP effects in the photolysis of solid acetone solutions in cyclohexane and assumed that spin polarization arises from recombination of contact radical pairs due to their T-S conversion. The present contribution gives the results obtained by studying nuclear polarization in the photolysis of a series of aldehydes and ketones in solid solutions. In our work we have been guided by the following considerations. The polarization of nuclear spins in photochemical processes is known to depend on the chemical (the routes of photochemical and photophysical transformations) and molecular dynamics of intermediates (radical pairs, triplet excited states, free radicals). Therefore, it seemed reasonable to perform the photolysis of various ketones when the system viscosity varied by many orders of magnitude to convert from nonviscous liquid into solid state. In this case, the chemical and molecular dynamics can undergo substantial changes. As a result, the temperature drop may cause e.g. the changes in the relative contribution of various mechanisms of nuclear polarization formation (S-To-mechanism, S-T-mechanism, triplet mechanism). Of particular interest was the influence of the energy transfer of electron excitation on the formation of nuclear spin polarization in the systems under study. We have studied the mechanism of the formation of spin polarization effects in the photolysis of a series of solid solutions of aldehydes and ketones. Unlike liquids, in solid solutions a diffusion mobility of radicals is either frozen or considerably slowed down. In the reactions of photodecomposition or photoabstraction in solid organic substances the radicals forming in the neighbourhood recombine (disproportionate) without escaping into the bulk. In this case, the conditions may appear for observing the S-T-(S-T+) mechanism of CIDNP formation. For some reactions important are not only the S-T mechanisms but also the S-To one. The relation between these mechanisms depends on the energy parameters of the reagents studied. It was established that in solid solutions active is the mechanism of spin diffusion that leads to redistribution of nuclear spin polarization between components. It is assumed that in both the solid and liquid solutions an important role in photochemical processes belongs to the energy transfer of electron excitation. This is confirmed by the dependence of the strength of CIDNP effects on UV flux, absorption cross-section, and the lifetime of triplet excited states of the reagents under study. It is established that the processes of energy transfer affect not only the routes of photochemical and photophysical transformations but also the molecular dynamics of radical pairs and excited states. This is observed by studying the CIDNP effects in the photodissociation of aldehydes and ketones in both liquid and solid solutions. Since a relative motion of radical atoms carrying spin density is rather complex in solid solutions, we have calculated the CIDNP effects for forward and rotational diffusion of radicals. The results of computational analysis show that the model of rotational diffusion of radicals most completely describes the experimental results.

ACKNOWLEDGEMENT. This work was sponsored by the Russian Foundation for Fundamental Researches (project 96-03-32956).

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POSTER 34

An Analysis of the CIDEP Mechanisms in the Hydrogen Abstraction Reactions of Excited Quinoxaline and Related Compounds

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Abstract

The Chemically Induced Dynamic Electron Polarization (CIDEP) mechanisms in the hydrogen abstraction reactions of excited azaaromatic compounds; quinoxaline, phenazine, and quinoline are investigated in detail. It is shown that several polarization mechanisms are involved and the observed CIDEP spectra vary strongly depending on various factors such as the concentration, the temperature, the delay time and the excitation light intensity. The net emissive spin polarization contributes dominantly to spectra at high concentrations and low temperatures, it is ascribed mainly to the radical-triplet pair mechanism (RTPM) between the produced radical and the precursor triplet. At a low concentration, the time evolution of the net component agrees reasonably with the prediction of the RTPM model, which indicates that the rise is mainly determined by the spin-lattice relaxation time (T_1^R) and the decay by the triplet lifetime. The RTPM usually gives a net E polarization of a slow rise and a slower decay compared with those of the TM and the geminate pair RPM. However, at high concentrations the emissive polarizations are found to show fast rises, maybe because the triplet lifetime is shortened less than T_1^R by triplet-triplet (T-T) annihilation as observed by transient absorption. The RTPM polarization is expected to play an important role generally, when the concentrations of triplet states and radicals are high and triplet states are relatively long-lived.

POSTER 35

A STUDY OF BENZOPHENONE PHOTOLYSIS IN SDS MICELLES IN THE PRESENCE OF 2,4,6-TRI-*tert*-BUTYL PHENOL BY ^{13}C TIME-RESOLVED SNP

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In recent years the techniques based on the indirect detection of magnetic resonance of radical intermediates, such as RYDMR, PYESR,etc. have gained wide acceptance. Stimulated nuclear polarization (SNP) [1] is among those type of techniques. The distinctive feature of this method is the detection of the NMR signals of reaction products in the presence of a microwave field. The shapes of the experimentally obtained SNP spectra and kinetics are depend on different parameters. Thus, splittings in the SNP spectra are determined mainly by the ratio A/Z [2], where A is the HFI constant and Z the rate of forced re-encounters. If $A/Z << 1$, the splitting is determined by the relative values of A, J - exchange interaction, and k_s - the reaction rate constant within the reaction zone. Since usually the value of J at the reaction sphere radius is expected to be very high, at $A/Z<< 1$ the splitting in the SNP spectra is reduced to one-half of the HFI constant. On the contrary, at $A/Z>>1$ the splitting should be independent of J and k_s, and just equal to the HFI constant A.

In this work, ^{13}C stimulated nuclear polarization (SNP) was applied to studying the photolysis of perdeuterated benzophenone in SDS micelles in the presence of 2,4,6,-tri-*tert*-butyl phenol with natural abundance of ^{13}C nuclei for both compounds. For RPs formed in this reaction, the HFI constants (0.7 mT - 2.6 mT) are much smaller than those for the RP investigated [2],which suggests that the SNP splitting is affected by the exchange interaction to influence in SDS micelles.

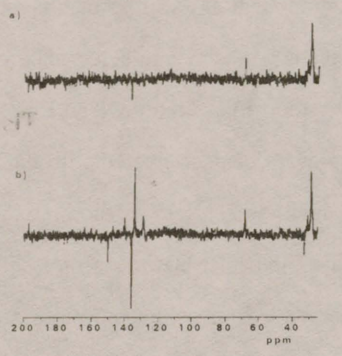

Fig.1

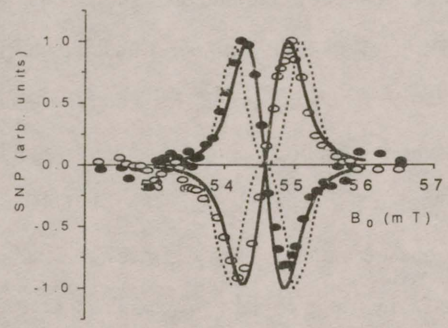

Fig.2

A detailed description of the experimental setup for detecting the SNP spectra and kinetics is given in detail elsewhere [1]. The ^{13}C NMR spectra of the reaction products obtained in the absence (a) and in the presence (b) of a resonance mw-field are shown on fig. 1. During the same experiment (i.e. under the same conditions) the SNP spectra and kinetics were detected for radical pairs with different positions of ^{13}C atom. All parameters of these pairs, except for the HFI constants, were identical, which allowed us to study the effect of the HFI constant on the relaxation and recombination processes in RPs. The ^{13}C SNP spectra are shown in fig. 2.

The time-resolved SNP and flash photolysis techniques were used to evaluate the rate constants of relaxation and escape from the micelle. The relaxation rate constants have been determined for radicals with various positions of the ^{13}C label, and the conclusions have been drawn about relevant relaxation mechanisms.

The experimental spectra have been simulated by the numerical solution of the stochastic Liouville equation as applied to the microreactor model. Based on the comparison of the experimental and simulated SNP spectra, the values of several ^{13}C HFI constants of the radicals formed in the reaction have been determined. The lower limit for the electron exchange interaction constant has been estimated at $|J_0|>40$ mT, which leads to a decrease in the splitting in the SNP spectra of the RPs under study.

Acknowledgment. This work was kindly supported by INTAS (Project No-93-1626) and Russian Science Foundation (Project N 96-03-32930).

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POSTER 36

EXPERIMENTAL AND THEORETICAL STUDY OF CIDNP EFFECT IN RADICAL PAIR RECOMBINATION AT SWITCHED WEAK MAGNETIC FIELDS

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Time Resolved CIDNP has been widely used to obtain detailed information about the kinetics of radical reactions and the spin dynamics of radical pairs. In TR CIDNP experiments, the delay between the laser flash and the detected rf-pulse is varied. The magnetic field used for CIDNP detection is determined by the resonance field of the NMR spectrometer and is thus restricted to high values. The first theoretical calculations of the geminate recombination probability at high magnetic fields under rapidly switched magnetic fields was performed for the first time in [1], where a new method of the investigation of CIDNP kinetics in a wide range of magnetic fields was proposed. The SEMF CIDNP method is based on the application of fast magnetic field switching during the lifetime of radical intermediates (radical pairs (RPs), biradicals, free radicals) and yields information about their spin dynamics and chemical kinetics. Our work experiments we applied SEMF CIDNP in different ways (with and without alternation of magnetic field direction) and to examine the possibility of this technique to yield quantitative information about the kinetics of RPs, biradicals, and free radicals.

A solution in a quartz cell positioned in the magnetic field B_0 of an auxiliary magnet was irradiated by UV light. A flow system was used to transfer the sample to the probe of a Bruker MSL-300 NMR spectrometer, where the NMR spectra of reaction products were detected. Helmholz coils provided a magnetic field B_s, which was parallel to B_0. The maximum field amplitude B_s was 20G, and the rise-time to switch the magnetic field was about 1 nsec. The essence of the SEMF CIDNP technique is the introduction of a variable time delay τ between the laser flash inducing the formation of RP and the edge of the B_s pulse. SEMF CIDNP kinetics is the τ dependence of the CIDNP signal intensity.

The switch of the additional magnetic field affects the nuclear polarization of diamagnetic molecules in different ways: it: (i) changes the spin dynamics conditions of the geminate and diffusing radical pairs; (ii) affects the value and sign of the electron and nuclear polarizations of free radicals as well as the rates of electron and electron-nuclear polarizations. Although the influence of SEMF through different mechanisms complicates the interpretation of experimental results, it opens a new possibilities of the investigation of the chemical kinetics and spin dynamics of short-lived intermediates at low magnetic fields. In particular, it allows (i) the investigation of the CIDNP kinetics of geminate RPs at weak magnetic fields with a very high time resolution; (ii) the variation of contributions of the geminate and diffusion RPs and (iii) the measurements of the electron polarization and cross-relaxation rates of free radicals at weak magnetic fields.

The possibilities of the new time-resolved method SEMF CIDNP to study the CIDNP kinetics in photochemical radical reactions in homogeneous and micelle solution at weak magnetic field have been demonstrated experimentally. The experimental ^{13}C CIDNP kinetics measured by SEMF at weak magnetic fields were obtained in the photolysis of benzophenone (D_{10}) and 2,4,6-tri-*tert*-bythyl phenol in SDS micelles with natural abundance of ^{13}C, and in the photolysis of benzoine labeled by carbonyl ^{13}C in the carbonyl. The CIDNP kinetics were obtained for 4 NMR lines, corresponding to RPs with different position of ^{13}C carbons. At low magnetic fields the CIDNP kinetics of short-lived biradicals formed during the photolysis of cyclododecanone and α,α-D_4-cyclododecanone in chloroform was measured by NMR lines corresponding to the α, β and γ protons and ^{13}C carbonyl atom.

The SEMF CIDNP kinetics were analyzed in terms of two theoretical approaches: numerical solution of the stochastic Liouville equation (SLE) and analytical matrix formula obtained in the balance approximation using the Green function formalism [1].

Acknowledgment. This work was kindly supported by INTAS (Project No-93-1626) and Russian Science Foundation (Project N-96-03-32930).

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POSTER 37

FLUORESCENCE-DETECTED MAGNETIC FIELD EFFECTS IN INTRAMOLECULAR EXCIPLEX SYSTEMS CONTAINING AZACROWN ETHER MOIETIES AS ELECTRON DONOR.

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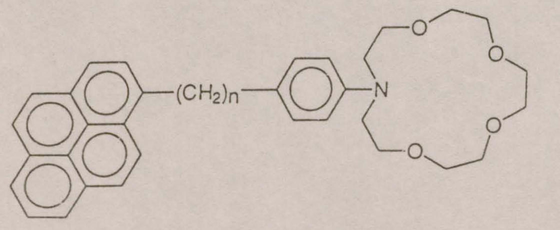
Introduction

Crown ethers containing nitrogen atoms in their macrocycle can act as electron donors in the process of photoinduced charge transfer with appropriate acceptors [1-4]. In particular, in the case of linked systems, homogeneous recombination of radical ion pairs generated is eliminated, so that the intramolecular (geminate) reactions are dominant [5,6]. Such flexibly linked compounds with azacrown moieties have been synthesized in this laboratory with the aim of studying the influence of metal ions on (i) the fluorescence quenching efficiency and (ii) the magnetic field effect (MFE) monitored via the fluorescence from the exciplex state (contact ion pair state) [5]. The nature of the magnetic field effect in linked radical pair systems and the importance of the intramolecular dynamics has been explored recently [6-8].

Compounds studied: Pyrene linked to azacrown ether (ACE) i.e. 13-[4-(n-Pyrene-1-yl-alkyl)-phenyl]-1,4,7,10-tetraoxa-13-cyclopentadecane



Py(n)ACE
n = 3, 9, 16

Results

(i) Metal ions form complexes with the macrocycle of the azacrown ether and affect the electron donor properties of the ACE, leading to a decrease of its quenching ability with respect to the linked excited pyrene, i.e., an increase of the primary (originally strongly quenched) fluorescence from the locally excited state of the pyrene moiety is observed. (ii) The saturation MFE (of the "hyperfine type") in radical ion pairs $^{3,1}(Py^- - ACE^+)$, detected via the exciplex fluorescence from $^1(Py^-ACE^+)^*$ is 40 % for n = 16 and 5 %

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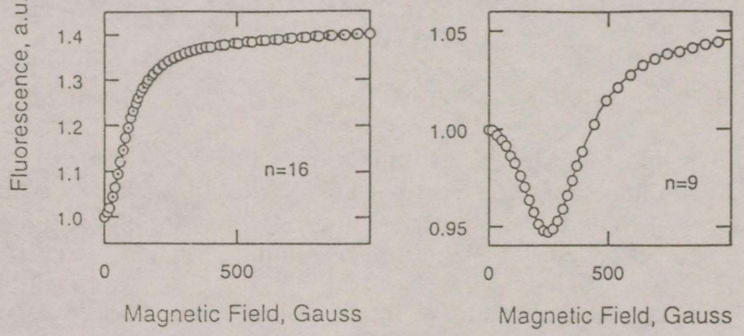

for n = 9. The latter system shows a pronounced J-resonance behavior at a field strength of ca. 245 Gauss. No MFE is detected for n = 3, as expected because of the large exchange interaction in the short-linked radical ion pair. In the cases n = 16 and 9 the MFE decreases upon addition of alkaline and alkaline earth perchlorates. This can be ascribed to an interaction between azacrown ether moieties and metal ions [9].

The observed photophysical/chemical features, (i) and (ii), suggest such A-D systems to be suitable for applications in solutions as metal ion sensors.

This work has been supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (Proj. Sta213/1-1). NKhP thanks the Max-Planck-Gesellschaft for providing a stipend and the Russian Foundation for Basic Research (Proj. 95-03-08864a) for financial support.

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POSTER 38

REACTIONS OF TRANSIENT Pt(III) COMPLEXES WITH AMINOACIDS

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It is well known that platinum in the stable Pt(IV) and Pt(II) valent states has the inert coordination sphere. However, the Pt(III) complexes with the extremely labile coordination sphere can occur as the intermediate species in the photoreduction of Pt(IV) complexes and can be used for the photosynthetic purposes.

The mechanism of $PtCl_6^{2-}$ photoreduction in organic solvents at room temperature is determined [1-3] by the following scheme of reactions

$$\begin{aligned} &PtCl_6^{2-} \xrightarrow{h\nu} (PtCl_6^{2-})^* \xrightarrow{RH} PtCl_6^{3-} + R + H^+ \\ &PtCl_6^{3-} \xrightarrow{\quad} PtCl_5^{2-} + Cl^- \\ &PtCl_5^{2-} \xrightarrow{\quad} PtCl_4^- + Cl^- \end{aligned}$$

Among the Pt(III) complexes only the $PtCl_5^{2-}$ complex has optical absorption (the bands with the maxima at 535 and 410 nm [1]). This absorption results from the primary $PtCl_6^{3-}$ complex dissociation and occurs fully 4 μs after a laser pulse. Since a precursor lifetime is very short, the presence of potential ligands usually has no effect on the formation of $PtCl_5^{2-}$ absorption. The rate constant of the coordination of bioorganic ligands with $PtCl_6^{3-}$ is evaluated to be $\leq 5\times10^6$ $M^{-1}s^{-1}$ and this reaction cannot compete with the process of $PtCl_6^{3-}$ dissociation to $PtCl_5^{2-}$ and Cl^-. Only for β-phenylalanine the coordination rate constant by an order of magnitude larger results in a significant decrease of $PtCl_5^{2-}$ yield in the presence of this aminoacid 4 μs after a laser pulse. The coordination with a platinum ion occurs via the oxygen atom of carbonyl group and for α-phenylalanine the steric difficulties created by the NH_3^+ group (zwitterion state of aminoacids) considerably decrease the rate constant in comparison with β-phenylalanine. It concerns tryptophan and proline. The β-phenylalanine reaction with $PtCl_6^{3-}$ occurs through the formation of the seven-coordinated intermediate $PtCl_6^{3-}$...L complex, which is transformed into the $PtCl_5^{2-}$...L complex during 10 μs with the chlorine ion ejected from the coordination sphere.

The presence of aminoacids in solution usually results in the acceleration of $PtCl_5^{2-}$ disappearance, the spectrum of which is replaced by that of the new $PtCl_5^{2-}$...L complex. In the 460-490 nm region, where $PtCl_5^{2-}$ does not practically absorb, it is possible to directly observe the kinetics of $PtCl_5^{2-}$...L optical absorption appearance. In the table the rate constants of the coordination some aminoacids with $PtCl_5^{2-}$ are submitted. The coordination of aminoacids with $PtCl_5^{2-}$ also occurs through oxygen of a carbonyl group.

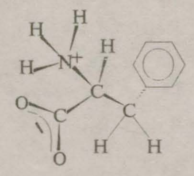
Practically in all cases the disappearance of the $PtCl_5^{2-}$...L complex occurs at the expense of the second aminoacid molecule introduction into the coordination sphere. The rate constants of this process are by about two orders of magnitude less than these of the first molecule introduction and lie in the $(1\text{-}3)\times10^4$ $M^{-1}s^{-1}$ range.

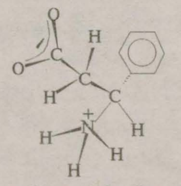
The final products of photochemical processes in the case of phenylalanines are the Pt(III) complexes with these aminoacids, that under further irradiation are transformed into the Pt(II) complexes. For tryptophan and proline the final products are the Pt(II) aminoacid complexes. Thus, the photochemistry can be a powerful tool of fast and effective preparation of the new Pt(II) complexes with many bioorganic ligands.

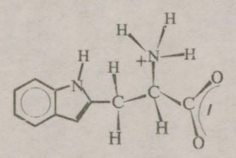
Table. The rate constants of aminoacids coordination with the Pt(III) transient complexes and the parameters of optical spectra of the $PtCl_5^{2-}$...L complexes.

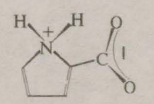
Pt(III) complex	Ligand	k, $M^{-1}s^{-1}$	λ_{max}, nm	ε, $M^{-1}cm^{-1}$	Ref.
$PtCl_6^{3-}$	β-Phenylalanine	6.9×10^7			5
$PtCl_6^{3-}$	α-Phenylalanine	$\leq6\times10^6$			5
$PtCl_5^{2-}$	Proline	1.9×10^6	490	2900	4
$PtCl_5^{2-}$	Triptophane	7.3×10^7	525	980	4
$PtCl_5^{2-}$	α-Phenylalanine	1.1×10^6	485	1750	5
$PtCl_5^{2-}$	β-Phenylalanine	2.2×10^6	485	1760	5

The structure of aminoacids used


α–Phenylalanine


β-Phenylalanine


Tryptophan


Proline

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POSTER 39

The role of radical ions in cis-trans isomerization of all-trans Retinal

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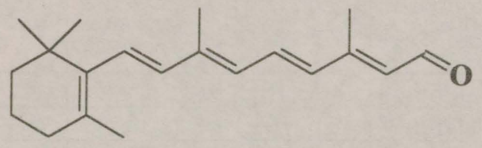
Retinal is known to be a chromophore of vision pigment rhodopsin. It is assumed that the act of cis-trans isomerization is involved in the formation of image in the mammalian eye. The role of radical ions in the processes of cis-trans isomerization of all-trans retinal (ATR) in the presence of electron donors and acceptors is the object of present study. This study employs ^1H CIDNP method, NMR analysis of isomer composition and INDO/AM1 calculation of geometrical and electronic structures of retinal radical ions.

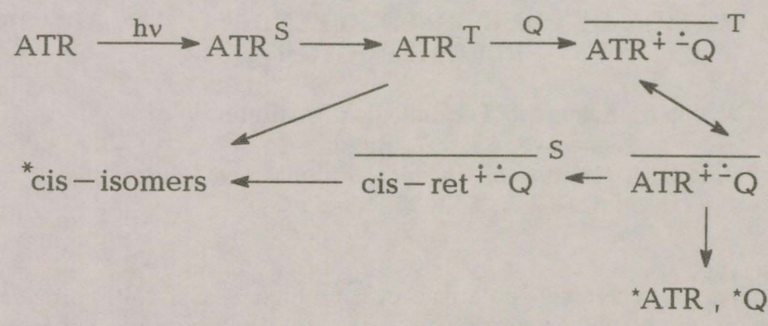


All-trans retinal

Under irradiation of ATR solutions in CD_3CN with electron donor (stilbene) and acceptors (2,5-dichlorobenzoquinone, chloranil) directly in the probe of NMR spectrometer we have observed the ^1H CIDNP effects of retinal and its isomers. The analysis of CIDNP effects has shown the formation of ATR radical anion in the photoreaction with stilbene and radical cation in the reaction with quinones. Comparison of CIDNP effects observed for ATR protons in the reactions with stilbene and quinones with the calculated hfi constants of ATR radical ions shows that they are in a qualitative agreement.

For reaction of ATR with trans-stilbene CIDNP effects were observed only in the case when light was absorbed by stilbene. In this case, we have observed only stilbene isomerization. Cis-stilbene polarized as a product of reverse electron transfer in triplet radical ion pair (RIP) of ATR anion radical and stilbene cation radical. The isomerization occurs in the "relaxed" triplet state of the stilbene [1].

In the reaction of ATR with quinones CIDNP effects were observed only for two quinones, whose redox potentials satisfy Weller-Zachariasse criterion for singlet electron transfer (SET) from ATR triplet excited state to quinone molecule: $E(RIP) < E_T(ATR) = 1.54$ ev. From the analysis of CIDNP effects in the reaction with quinones we have concluded that ATR and the products - cis isomers have been polarized as cage products of singlet RIP with triplet precursor. CIDNP dependence on ATR concentration point out, that electron transfer is the main decay chanel of retinal triplet state. This implies, that the isomerization may proceed in radical ion pair, too.



In fact, this hypothesis means, that the isomerization occurs in radical cation itself. There is widely discussed viewpoint in the literature [2], that isomerization occurs in so-called "twisted triplet" (cf. with "fantom triplet" formed in stilbene isomerization [1]). We suggest that "twisted triplet" leads to radical cation with the same geometrical configuration, followed by its further transformation to cis-isomers.

The additional support of this hypothesis is the experimental result, that the composition of isomers formed under UV-irradiation of ATR in the presence of quinones differs from that performed in the direct photolysis of all-trans retinal. Unlike the conclusions drawn in [2] the change in the composition of isomers cannot be explained by the processes of energy transfer from quinone molecules in the excited triplet state to retinal. In our experiments the light is mainly absorbed by retinal itself.

Thus, the influence of quinone on cis/trans ratio and isomer CIDNP effects allow us to suppose the photoisomerization of ATR in radical ion pair. Another possibility is isomerization in exciplex, obtained from ATR in triplet state and molecules of quinone. Now we cannot choose between these hypothesis.

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POSTER 40

CALCULATION OF CIDNP FIELD DEPENDENCES IN BIRADICAL RECOMBINATIONS.

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Studies of chemical polarization of nuclei (CIDNP) provide ample information about the mechanisms and molecular-kinetic parameters of reactions, as well as about magneto-resonance parameters of the reacting particles. Investigation of geminate recombination processes in molecular-organized systems, such as biradicals, micellized radical pairs (RP), clusters in the gas phase, etc., by this method is of great interest. Paper [1] reports the analysis of CIDNP field dependences of acyl-alkyl biradicals in weak magnetic fields at different concentrations of acceptors the role of which reduces to the decrease in the mean RP lifetime.

The present paper presents the calculation of CIDNP in weak magnetic fields with allowance for all singlet-triplet transitions essential for long-lived systems, including S-T_ transitions in the terms intersection zone. The influence of the acceptor concentration C_s has been studied by varying the mean RP lifetime.

The approach is based on the kinematic approximation in the theory of magnetic and spin effects. In the framework of this approximation the probability w of singlet RP recombination with the given configuration {m} of nuclear spins in the case of triplet precursor is defined by the expression

$$w_m^T = \frac{U(\tau_p - \tau_m)}{3(1 + U\tau_m)}, \quad \tau_m = \left(\hat{\hat{g}}\right)_{SmSm,SmSm},$$

where U is the rate constant of contact RP recombination in the singlet state; τ_p is the mean residence time of reactants in the reaction zone ("u"); $\tau_m = \left(\hat{\hat{g}}\right)_{SmSm,SmSm}$ is the element of the evolution matrix $\hat{\hat{g}}$ defining the residence time of RP in the zone "u" in the singlet state with the configuration {m} of nuclear spins on condition that the start was from the same zone "u" and in the same state.

Calculation of the evolution operator $\hat{\hat{g}}$ requires that the Liouville equation be solved which is a complicated problem. However, some simplifying assumptions concerning the mechanisms of spin transitions allow this problem to be successfully solved. S-T_ transitions in the terms intersection zone ("c") can be taken into account in the balance approximation by defining the effective form of this zone. In view of the short-range nature of the exchange interaction, the following expression is obtained for $\hat{\hat{g}}$ [2]

$$\hat{\hat{g}} = \hat{\hat{\Lambda}}\left(1 + i\hat{\hat{K}}_J\hat{\hat{\Lambda}}\right)^{-1}, \quad \hat{\hat{\Lambda}} = \hat{\hat{g}}_0 - \hat{\hat{g}}_{0uc}\left(1 + \hat{\hat{K}}_c\hat{\hat{g}}_{0cc}\right)^{-1}\hat{\hat{K}}_c\hat{\hat{g}}_{0uc},$$

where $\hat{\hat{K}}_J$ is the matrix of the exchange interaction constants, and $\hat{\hat{K}}_J$ is the matrix of transitions between intersecting terms in the balance approximation proportional to the probability of finding RP in the zone "c".

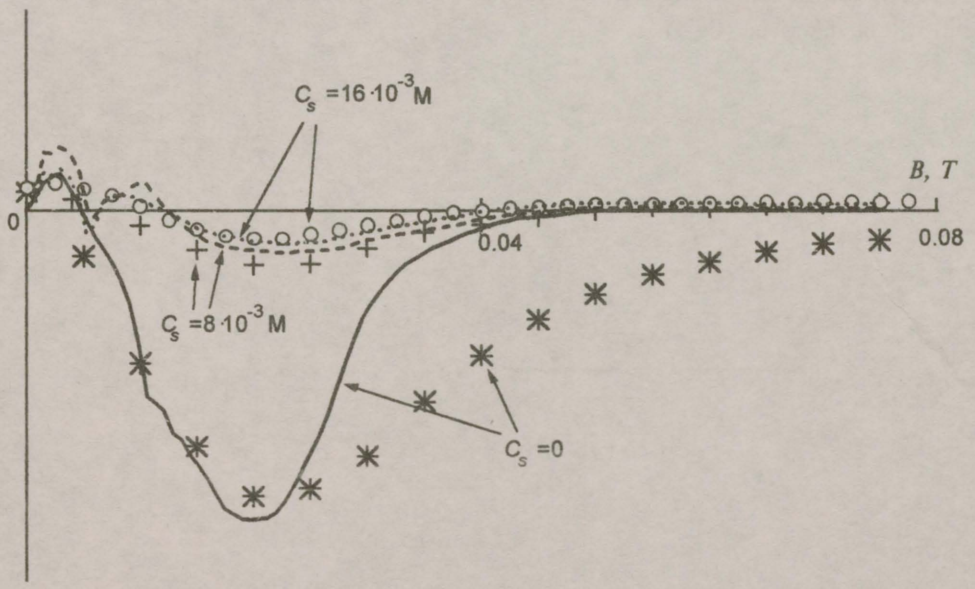
The Liouville matrix $\hat{\hat{g}}_o$ has the same meaning as the matrix $\hat{\hat{g}}$ in the case where the spin evolution is determined solely by the coordinate-independent part of the spin-Hamiltonian H. $\hat{\hat{g}}_{0uc}$ and $\hat{\hat{g}}_{0cc}$ are the mean values of RP spin evolution operator in the zone "c" on condition that the start was from the zone "u" and from the zone "c", respectively. These matrices are also defined by the coordinate-independent part of H.

In order to calculate CIDNP of acyl-alkyl biradicals, we have introduced one more simplification, namely, we have taken that $\hat{\hat{g}}_o \approx \hat{\hat{g}}_{0uc} \approx \hat{\hat{g}}_{0cc}$ which is justified by the closeness of the zones "c" and "u".

Comparison of theoretical results and experiment for α-protons of $C_{11}H_{20}O$ biradical is given in the figure. The mean lifetime of the biradical u^{-1} was determined by the decay rate on acceptors from the relation

$$u = u_o + k_s C_s,$$

where u_o^{-1} - the intrinsic lifetime of RP - was taken equal to 10^{-6} s; $k_s = (2.3 \pm 0.4) \cdot 10^9\ M^{-1}c^{-1}$ [1].



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POSTER 41

STUDY OF FLUORESCENCE-DETECTED MAGNETIC FIELD EFFECT IN SOLUTIONS CONTAINING P-PHENYLENEDIAMINE DERIVATIVES

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During the last two decades several research groups made some efforts to investigate the magnetic field effect (MFE) on fluorescence of systems producing radical ion pairs (RIP) or exciplexes respectively via photoinduced electron transfer reactions. A small applied external magnetic field affects only the field-sensitive spin evolution process which interconverts the spin multiplicity of the spin-correlated RIP intermediates. But nevertheless this phenomenon provides the possibility of changing the reaction pathways.

A self-built modulation technique MARY-apparatus (MAgnetic field effect on Reaction Yield) will be described (fig.1).

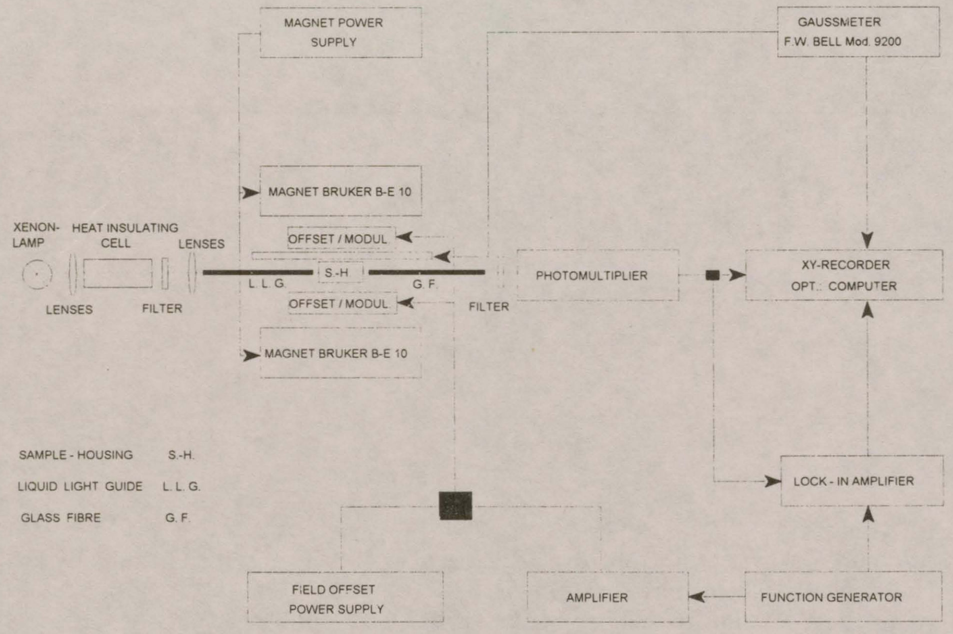

Fig.1: A block diagram of the MARY-apparatus

The preliminary results of our investigations on the magnetic field effect on the luminescence of various highly purified N,N,N´,N´-tetraalkyl-p-phenylenediamine derivatives (alkyl = methyl, ethyl, n-propyl, i-propyl) in solvents of different dielectric constants and/or binary solvent mixtures are reported.

Further research is concerned with the applicability of MARY-spectroscopy to electron self-exchange reactions in solution via the $B_{1/2}$-dependence on the concentration of the electron donor (D) in order to determine the electron self-exchange rate constant k_{ex} (eq.1).

$$D + D^{+\cdot} \overset{k_{ex}}{\rightleftarrows} D^{+\cdot} + D \qquad (1)$$

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U. E. STEINER AND T. ULRICH; *Chem. Rev.*, 1989, **89**, 51.
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POSTER 42

Quantitative Time-Resolved EPR.
Determination of the CIDEP and kinetic parameters of the cumyl radical obtained by direct photolysis of *trans*-azocumene.

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Chemically Induced Dynamic Electron Polarization (CIDEP) of the cumyl radical generated by direct laser flash photolysis of azocumene in low viscous solution is investigated by time-resolved cw EPR spectroscopy [1].

According to the fact , that azocumen decays from an excited singlet state, the spectrum at short times (fig. 1a) exhibits an A/E polarization pattern due to RPM in the geminate radical pair. The absence of net polarization indicates that the life time of the cumyldiazenyl radical which is formed if azocumene decomposes stepwise [2], is much smaller than its relaxation times (<< 10-50ns [3]). At longer times (fig. 1b) the F-pair polarization dominates and results in a phase inversion to an E/A multiplet, which decays on the 100μs time scale.

The EPR time profiles are analysed in terms of modified Bloch equations. In order to receive precise informations about the photochemistry of azocumene and about the cumyl radical system, the relaxation times of the cumyl radical and parameters of the spectrometer are measured in separate experiments. The microwave magnetic field strength is obtained by evaluation of the torrey oscillations in the 2-cyano-2-propyl and cumyl radical systems. The spin-spin and spin-lattice relaxation times are determined from the saturation behavior of the time-resolved EPR linewidth and from torrey oscillations. The scaling factor (signal/magnetization) is determined by a probe of persistent radical.

The analysis of the EPR time profiles, taken with a variety of different absorbed laser light intensities and microwave field strengths shows the following:

1. The photolysis of *trans*-azocumene proceeds via two distinct mechanisms, direct photocleavage of the *trans*-isomer and thermal decomposition of the photochemically formed *cis*-isomer.
2. The life time of *cis*-azocumene is found to be 14±3μs at 293K in benzene, which is about two times larger than has been obtained in a previous flash photolysis study [4].
3. The quantum yield of free radicals, escaping from the primarily cage, is found to be 0.14±0.03 for the decay of the excited *trans*-azocumene and 0.18±0.04 for the thermal decay of *cis*-isomer.
4. The geminate RPM polarization is considerably smaller than the F-pair polarization.

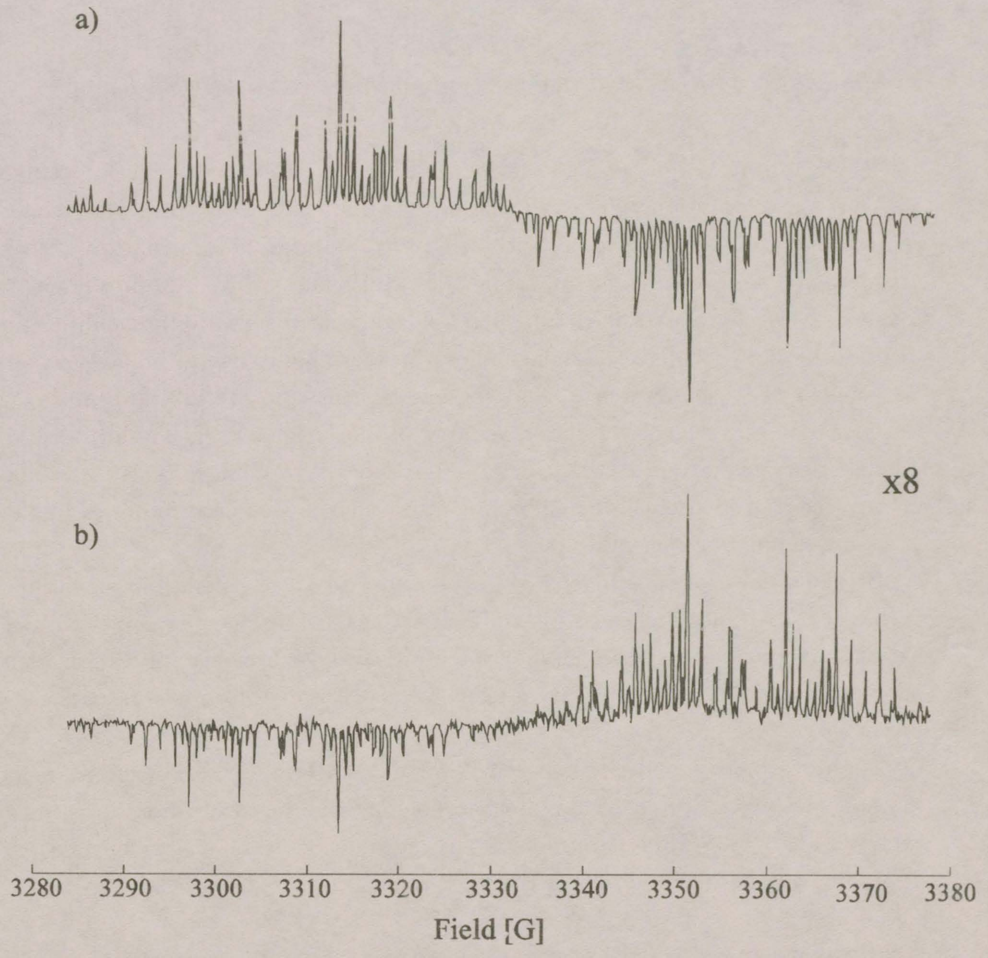

Figure 1. Time-resolved EPR spectrum of the cumyl radical generated by laser flash photolysis of *trans*-azocumene: a) 3μs, b) 50μs after laser excitation.

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POSTER 43

LEVEL-CROSSING (MARY) SPECTROSCOPY OF ION RADICAL PAIRS.

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The study of MAgnetic field effects on Reaction Yield of chemical reactions (MARY-spectroscopy) provides valuable information on short-lived spin-correlated radical ion pairs. As has been recently demonstrated, the coherent nature of radical ion pairs can result in the appearance of additional local fluorescence intensity maxima at level-crossing fields [1]. This phenomenon opens the possibilities for identification of short-lived paramagnetic species forming in nonpolar solutions under ionizing radiation as well as studying of reactions they are involved in. Using this technique the signals of cation radicals of *cis*-decalin, *trans*-decalin, tetramethylethylene, triethylamine, $\Delta_{9,10}$-octalin (decalene) etc., anion radicals of hexafluorobenzene, tetrafluorobenzene and many other species were detected in non-polar solutions at room temperatures [1].

Breaking down of spin coherence in the course of (i) degenerate ion-molecular exchange [2], (ii) intramolecular dynamic transitions, (iii) exchange interaction with external paramagnetic species [3] makes the MARY-lines broaden and vanish, thus allowing one to study the mentioned phenomena. Examples for reactions (i-iii) are presented.

The direct correspondence between ESR and MARY-spectra is revealed, making possible to get ESR spectrum of corresponding counter-ion without microwave excitation (Fig. 1)! Time-resolution of this technique depends on *hfi* constant A_{hf} of probing counter-ion and falls in the units of nanosecond time scale.

Acknowledgement. This work was performed under the auspices of INTAS Grant #93–1626.

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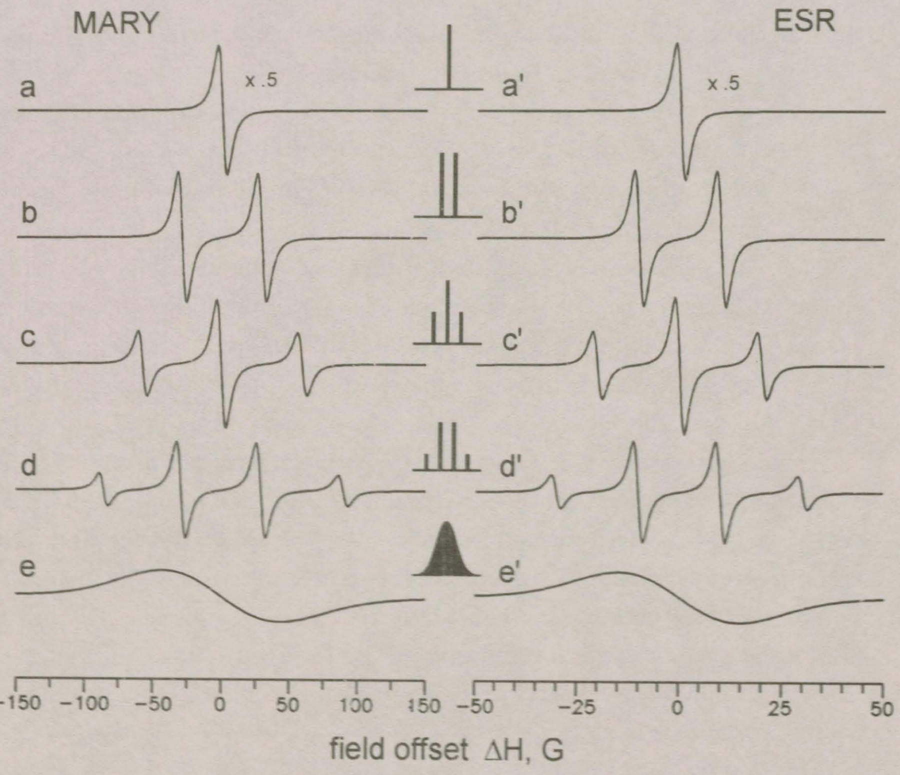

Figure 1: Correspondence between MARY (left) and ESR (right) spectra for ion radicals with different hfi substructure (theory). HFI parameters of examined ion: (a, a′) – no hfi; (b, b′) – 20G(1H); (c, c′) – 20G(2H); (d, d′) – 20G(3H); (e, e′) – $2\Delta^2$=20G. Parameters of probing counterion (MARY) A_{hf}=1000G(4H), recombination linewidth (hwhm) is 2G. MARY spectra centered at $H^* = 3A_{hf} = 3000$G. Field offset scaled triple for MARY spectra to get visual coincidence with corresponding ESR spectra. Note that no microwave field applied in case of MARY.

POSTER 44

MAGNETIC FIELD AND MAGNETIC ISOTOPE EFFECTS ON THE LIFETIMES OF CHAIN-LINKED BIRADICALS

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In the last years, magnetic field effects (MFEs) and magnetic isotope effects (MIEs) on radical pairs and biradicals have been studied mainly in relatively low magnetic fields (≤ ca. 1 T). In this paper, we report the MFEs (≤ ca. 13 T) and MIEs on the lifetimes of triplet biradicals generated from the intramolecular hydrogen abstraction reaction of bifunctional chain molecules.

Figure 1 shows the MFEs on the lifetimes of triplet biradicals generated from the chain molecules shown in the figure. All the biradicals exhibit significant MFEs. In the case of the ^{13}C-substituted biradical remarkable MIEs are observed in the magnetic field region between 0T and ca. 4 T, whereas the duterated biradical exhibits little MIEs.

The MFEs are interpreted in terms of the relaxation mechanism. The significant MIEs in the low magnetic field region (≤ ca. 4 T) indicate that spin relaxation among spin sublevels are primarily controlled by the *anisotropic* hyperfine interaction, contribution of the dipole interaction being of minor. In the higher region (≥ ca. 4 T), the relaxation is chiefly controlled by the *anisotropic*Zeeman interaction.

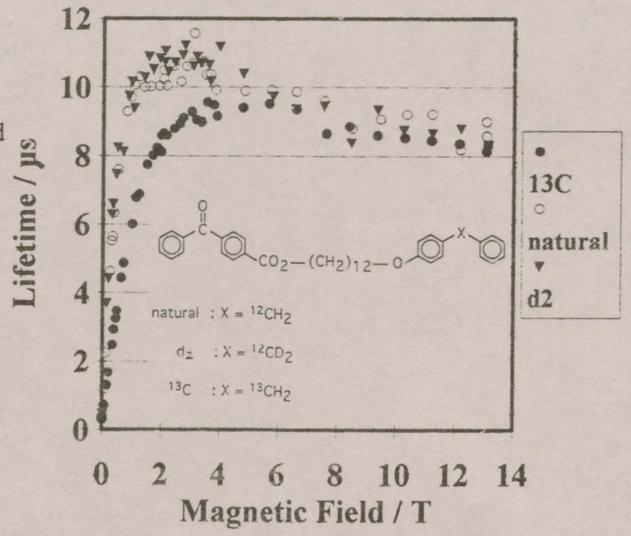

Fig. 1. Magnetic field dependence of biradical lifetimes.

POSTER 45

EPR of the primary radical pair in reaction centres of photosynthetic bacteria

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The primary steps of photosynthesis in purple bacteria can be summarized as follows:

$$PIQ \rightarrow P^{*}IQ \rightarrow P^{\cdot+}I^{\cdot-}Q \rightarrow P^{\cdot+}IQ^{\cdot-}$$

where P is the primary electron donor, I is a pheophytin, the primary acceptor, and Q a quinone, the secondary acceptor. Electron transfer from the primary donor to the pheophytin is very fast (~3 ps). In contrast to the primary radical pair, which exists for ~200 ps, the secondary radical pair $P^{\cdot+}Q^{\cdot-}$ has a lifetime of ~100 μs and can easily be observed by EPR. Prereducing or removing the quinone blocks the second electron transfer step, prolonging the lifetime of the primary radical pair and allowing the triplet state of the primary donor, ^3P, to be formed.

Proskuryakov *et al.* [1] have detected a new signal at g=2, using time-resolved continuous wave EPR, that decays with a time constant equal to the rise time of ^3P (38 ns in *Rhodobacter sphaeroides (Rb. sph.)* R26 reaction centres (RC's) with the quinone pre-reduced and 53 ns with the quinone removed; 10 ns for *Rhodopseudomonas (Rps.) viridis* RC's). This suggests that the new signal is due to the precursor of ^3P, i.e. the triplet state of $P^{\cdot+}I^{\cdot-}$. The spectra are polarized: absorptive at low field and emissive at high field, broad (35–70 Gauss) and relatively featureless.

A preliminary interpretation [1] in terms of the Spin Correlated Radical Pair (SCRP) model [2], which has been succcessfully applied to $P^{\cdot+}Q^{\cdot-}$, gave estimates of J, the exchange interaction of $P^{\cdot+}$ and $I^{\cdot-}$, and k_T, the rate of $^3[P^{\cdot+}I^{\cdot-}] \rightarrow {}^3P$.

Here we describe a modified version of the SCRP model more appropriate to $P^{\cdot+}I^{\cdot-}$. The changes to the model are based on the following differences between the primary and secondary radical pairs:

1. The electron-electron interactions within the secondary radical pair are weak, so that a gaussian broadening can be used to take into account the unresolved hyperfine interactions. In contrast, the interactions in the primary radical pair are larger, necessitating a fuller treatment of the hyperfine couplings by averaging over distributions of resonance frequencies of the two electron spins.

2. The lifetime of $P^{\cdot+}I^{\cdot-}$ is much shorter than that of $P^{\cdot+}Q^{\cdot-}$, so that (Lorentzian) lifetime broadening must be introduced. As the various spin states of the radical pair have different singlet and triplet character, and the singlet and triplet states have different lifetimes, the EPR transitions are broadened to different extents.
3. The populations of the spin states of $P^{\cdot+}I^{\cdot-}$ must be adjusted to include the depopulation rates ($k_S \neq k_T$).

The spin-polarized spectra of $P^{\cdot+}I^{\cdot-}$ in *Rb. sph.* R26 and *Rps. viridis* have been satisfactorily simulated, as have the kinetics of the disappearance of $P^{\cdot+}I^{\cdot-}$ and formation of ^3P. An extension of the model to include the exchange and dipolar interactions between $I^{\cdot-}$ and Q^{-} is used to describe the kinetics of ^3P formation in pre-reduced RC's of *Rb. sph.* R26.

Acknowledgement

We are indebted to Prof. Ivan Prokuryakov for communicating his r[illegible]ts prior to publication.

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POSTER 46

OSCILLATING MAGNETIC FIELD EFFECTS ON THE YIELDS OF RADICAL PAIR REACTIONS

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The effects of fluctuating magnetic fields on the yields of chemical reactions are explored within the radical pair mechanism. Approximate analytical expressions and exact numerical calculations are used to investigate the origin of the oscillating magnetic field effect (OMFE) and its dependence on radical pair lifetime, magnetic field strength and frequency (see Figure 1). The validity of the analytical expressions as a function of these parameters is discussed. For the case of a single nucleus the principal effect of the oscillating field occurs, as expected, when the radiofrequency, ω_{rf}, matches the hyperfine coupling, a; magnetic field effects of up to 25 % can be found when the singlet-triplet interconversion induced by the oscillating field is much faster than the rate of reaction of the radical pair (it is assumed that the rate constants for the reaction of singlet and triplet radical pairs are equal). The field effect decreases when more nuclei are present in the system, but is still found to be about 15% for the case of three inequivalent nuclei. This relatively small reduction arises form the overlap of the various resonances caused by lifetime broadening and off-resonance effects. In the case of two or more inequivalent nuclei the resonances do *not* in general appear at the frequencies of the hyperfine couplings.

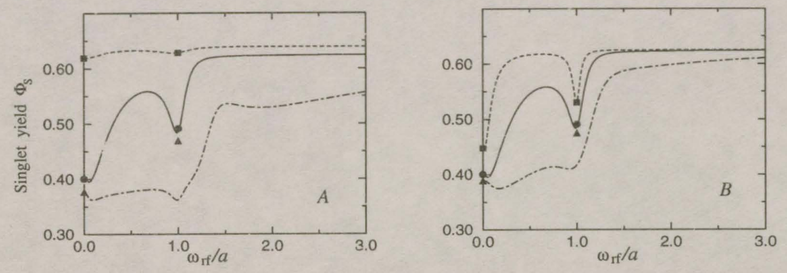

Figure 1: Singlet product yield Φ_S for a one-nucleus radical pair as a function of the frequency ω_{rf} of an oscillating magnetic field. (A) $\gamma B_1 = 0.125a, 2\pi k = 0.0125a$ (dash-dot line), $0.125a$ (solid line), $1.25a$ (dashed line), (B) $2\pi k = 0.125a, \gamma B_1 = 0.0625a$ (dashed line), $0.125a$ (solid line),$0.25a$(dash-dot line). The squares, circles and triangles give the values of Φ_S obtained using the analytical expressions. (k = rate constant with which radical pair disappears, B_1 = strength of oscillating field, a = hyperfine coupling)

Finally, the influence of a small static magnetic field, B_0, is investigated distinguishing between the effects of left and right circularly polarised radiofrequency fields. Results for the case of $\gamma B_0 = a/16$ with B_0 being of a similar size to the geomagnetic field are presented. The corresponding numerical results for the case of a linearly polarised radiofrequency field are presented.

The likelihood of observing the OMFE experimentally is discussed.

POSTER 47

REGISTRATION OF SUPERFAST HOLE MOTION IN IRRADIATED ISOOCTANE BY QUANTUM BEAT TECHNIQUE

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The irradiation of solutions results in free electrons and solvent holes. In the presence of acceptors the electrons and holes are scavenged forming secondary radical ion pairs. Because of the conservation of spin angular momentum the radical ion pair arises in nonstationary coherent singlet state. In the external magnetic field the singlet-triplet dynamic transitions take place for spin-correlated pairs and this process manifests itself in quantum beats in recombination fluorescence due to electron transfer from electron acceptor anion (in our instance it is *p*-terphenyl-d_{14}) to hole acceptor cation (diphenylsulfide-d_{10}). The electrons are scavenged fast enough due to their high mobility whereas the holes are captured in much slower reactions limited by molecular diffusion. A delay in formation of hole acceptor radical cation is the cause of phase shift in the quantum beats. The value of phase shift is connected with a hole capture rate constant by the expression [1]:

$$\omega \cot \varphi = \tau_0^{-1} + k[D] \qquad (1)$$

where $[D]$ is diphenylsulfide concentration, τ_0 is a hole life-time, k is a hole capture rate constant, φ is a phase shift and ω is a difference of Larmor frequencies for solvent hole and diphenylsulfide cation. As it follows from experimental data for a series of alkane solutions k values exceed diffusion-controlled one ($k=(1\div5)\times10^{10}$ M^{-1}s^{-1}). The life-time of solvent holes has been estimated ($\tau_0>20$ ns) from cut-off in experimental dependence $\omega \cot \varphi$ *via* diphenylsulfide concentration.

The system (diphenylsulfide-d_{10})$^+$/(*p*-terphenyl-d_{14})$^-$ is the most favorable to observe quantum beats due to simple EPR spectra and a large *g*-factor difference ($g_{DPS^+}-g_{PTP^-}=0.0056\pm0.0002$) of partners. Unfortunately, other available hole scavengers have *g*-factor values almost the same as for (*p*-terphenyl-d_{14})$^-$ one, and very strong magnetic fields are needed to observe quantum beats in this case.

We propose the next approach to solve this problem. Addition of hole acceptors other than diphenylsulfide in irradiated solution of diphenylsulfide-d_{10} and *p*-terphenyl-d_{14} should lead to farther diminish of phase shift in quantum beats of (diphenylsulfide-d_{10})$^+$/(*p*-terphenyl-d_{14})$^-$ radical ion pair due to a hole capture by the second acceptor. The expression (1) in this case can be readily modified:

$$\omega \cot \varphi = \tau_0^{-1} + k_1[A] + k[D] \qquad (2)$$

If one keeps the diphenylsulfide concentration constant and varies the concentration of the second acceptor, the slope of experimental line will give the hole capture rate constant for the latter (Fig. 1). The opposite case (fixed concentration of an additive and varied diphenylsulfide concentration) gives the opportunity to obtain the rate constant for the second acceptor from cut-off of experimental line (Fig. 2).

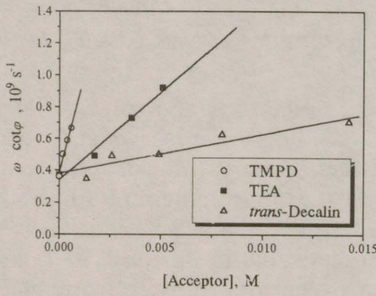

Figure 1. Irradiation of isooctane solutions of diphenylsulfide-d_{10} (12 mM) and p-terphenyl-d_{14} (1 mM) in the presence of N,N,N',N'-tetramethyl-p-phenylenediamine, triethylamine and *trans*-decalin.

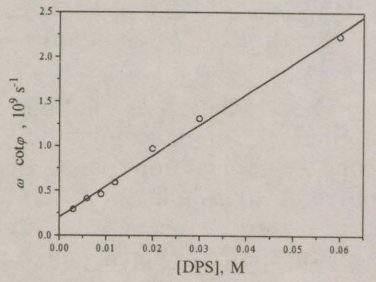

Figure 2. Irradiation of isooctane solution of diphenylsulfide-d_{10} and p-terphenyl-d_{14} (1 mM) with addition of 1.8 mM triethylamine.

The hole capture rate constants obtained by this method were as follows: 4.9×10^{11} (TMPD), 1.2×10^{11} [from the slope, Fig.1] and 1.1×10^{11} [from the cut-off, Fig. 2] (TEA), 2.5×10^{10} (*trans*-decalin) and 3.5×10^{10} M^{-1}s^{-1} (diphenylsulfide-d_{10}). These values substantially exceed diffusion controlled ones for isooctane (~10^{10}) and this behavior of isooctane is similar to cyclic alkanes with six-membered ring [2].

Acknowledgment. The financial support of INTAS (Grant No. 93-1626) and Russian Foundation for Basic Research (Grant No. 96-03-33694a) is gratefully acknowledged.

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POSTER 48

HOLE CAPTURE IN IRRADIATED ALKANES STUDIED BY QUANTUM BEATS TECHNIQUE

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Dynamic transitions between levels of different multiplicity are known to occur in spin-correlated radical pairs produced in solutions by light or ionizing radiation. The initial coherent state of a radical pair being nonstationary, singlet-triplet (**S-T**) beats arise in the system [1]. Beats induced by g-factor difference have been recorded for the (diphenylsulfide-d_{10})$^+$/(p-terphenyl-d_{14})$^-$ {(DPS)$^+$/(PTP)$^-$} radical ion pairs [2]. In strong magnetic field the transition frequencies coincide with the differences in the EPR frequencies of pair partners ($\omega = \Delta g\beta H\hbar^{-1}$). The partners in this system are the species with simple EPR spectra and large g-factor difference, favorable to observe quantum beats of large amplitude.

The quantum beats phenomenon could be employed to study the process of charge transfer from primary solvent holes (S$^+$) to solute molecules [3]. The ionization of a dilute solution results in a free electron and a solvent hole. Due to their high mobility the electrons are scavenged by PTP fast enough, whereas the holes are captured in much slower reactions that are assumed to be limited by molecular diffusion. As a result, beats in the secondary radical ion pair should start with a delay. The delay in (DPS)$^+$ formation leads to a phase shift in quantum beats and related decrease of their amplitude [3].

The value of phase shift φ was shown to be determined by the capture rate constant k, the hole decay time τ_1 and g-factor shift upon hole capture,

$$(\tau_{cap})^{-1} = \omega_{12} \cot\varphi = (\tau_1)^{-1} + k[DPS] \qquad (1)$$

Consequently, the hole capture and decay could be extracted from the slope and cut-off of the concentration dependence.

The experimentally obtained dependence $(\tau_{cap})^{-1}$ on DPS concentration for a series of alkane solutions is shown in Fig.1.

Table 1. Solvent hole rate constants $S^+ + DPS \xrightarrow{k} S + DPS^+$

Solvent	k, 10^{10} M^{-1}s^{-1}	η (20°), cP	k_d, 10^{10} M^{-1}s^{-1}	k/k_d
Hexane	2.3	0.31	2.1	1.1
Isooctane	3.3	0.50	1.3	2.5
Cyclohexane	4.1	0.98	0.7	5.9
n-Dodecane	0.8	1.34	0.5	1.6
trans-Decalin	2.8	2.13	0.3	9.3
cis-Decalin	1.9	3.38	0.2	9.5
Squalane	0.7	21.1	0.03	23

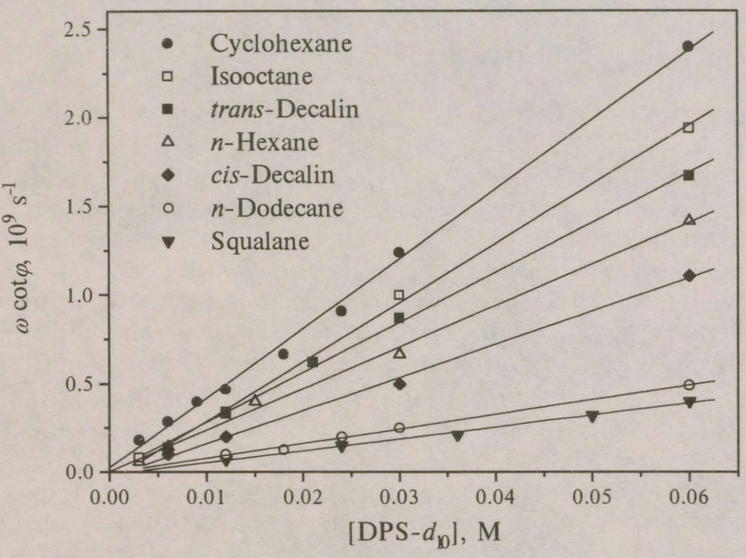

Figure 1. Dependencies of $(\tau_{cap})^{-1} = \omega \cot\varphi$ on diphenylsulfide-d_{10} concentration for a series of alkanes in the presence of 1 mM *p*-terphenyl-d_{14}.

As seen from the table, the rate constants of hole capture by DPS *k* for all alkanes studied exceed diffusion-controlled ones $k_d=(8kT/3\eta)$ estimated from solvent viscosities. The effect is more significant the more viscous the solvent is. This excess can be related to a large radius of charge transfer between solvent hole and acceptor because such a reaction can follow the tunneling mechanism or to a high hole mobility due to hopping mechanism.

Acknowledgment. The financial support of INTAS (Grant No. 93-1626) and Russian Foundation for Basic Research (Grant No. 96-03-33694a) is gratefully acknowledged.

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POSTER 49

SIMILARITY OF THE MAGNETIC FIELD DEPENDENT RADICAL PAIR RECOMBINATION IN PHOTOSYSTEM II AND BACTERIAL REACTION CENTERS - CONCLUSIONS ON STRUCTURE AND ENERGETICS

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In $D_1D_2Cytb_{559}$ reaction centers (RCs) of Photosystem II (PSII) the radical pair $P680^+Pheo^-$ recombines on the ns-time scale to the singlet groundstate with the rate k_S or, after hyperfine induced singlet-triplet-mixing (STM), to the triplet state $^3P680^*$ with the faster rate k_T, in full analogy to the intensively studied radical pair recombination in bacterial RCs [1]. An external magnetic field hinders STM, thus reducing the yield Φ_T of $^3P680^*$ and slowing the recombination. The decrease of Φ_T with increasing magnetic field yields a characteristic lineshape with a halfwidth $H_{1/2}$ governed mostly by lifetime broadening of the radical pair states.

The recombination of $P680^+Pheo^-$ and the decay of $^3P680^*$ were monitored via transient absorbance changes at 681nm and 544nm between 1ns and 10ms [2]. Monoexponential fits of the $P680^+Pheo^-$ recombination yield time constants of ≈100ns at 0G and ≈170ns at 700G at 90K, reducing to 50ns and 65ns at 290K. These values are slightly larger than the radical pair lifetimes in bacterial RCs. Deviations of the radical pair recombination from monoexponentiality were observed, analogous to those found in bacterial RCs. These arise from the statistical orientation of the nuclear spins, resulting in a distribution of the frequency of hyperfine induced STM, which in turn leads to a distribution of radical pair lifetimes [3]. The residual transient absorbance after completion of radical pair recombination is a measure for Φ_T. From the magnetic field dependence of Φ_T, $H_{1/2}$ was found to have a temperature dependent value of 200-340G, which is larger than in bacterial RCs by a factor of approx. 5.

From the radical pair lifetimes and Φ_T it can be concluded that the singlet recombination rate k_S in PS II is significantly smaller than in bacterial RCs. The larger value of $H_{1/2}$ in PS II, on the other hand, indicates a larger value of the triplet recombination rate k_T. Due to this larger difference between k_S and k_T in PS II, the effects of the STM-frequency distribution, which causes a distribution of radical pair lifetimes τ_{RP} ranging from $2/(k_S+k_T) \approx 2/k_T$ to $1/k_S$, are much more pronounced than in the bacterial RC. The expected distribution of τ_{RP} for values of k_S and k_T similar to those found in PS II is shown in Fig. 1. Clearly, the concept of a well defined radical pair lifetime has to be abandoned for PS II. Even the determination of an average radical pair lifetime $<\tau_{RP}>$ is not possible, since slow components with very long lifetimes but small amplitudes (thus difficult to detect) contribute significantly to $<\tau_{RP}>$. This severely hinders the accurate determination of k_S. Only explicit numerical simulations of the recombination dynamics **and** the magnetic field dependence of Φ_T allow the correct determination of k_S in PS II, giving values which are smaller than in bacterial RCs by a factor of 50. This difference reflects the larger free energy gap between the radical pair and the ground state due to the different redox potentials of the pigments of PSII and bacterial RCs.

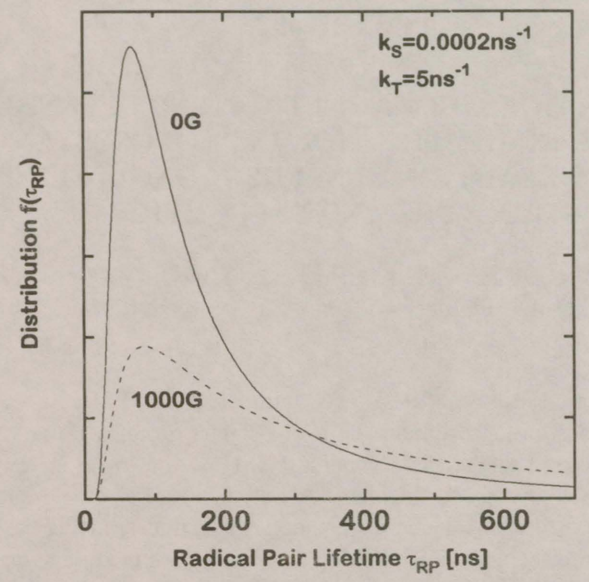

Fig. 1: Simulation of the radical pair lifetime distribution at 0 and 1000G in PS II caused by the inherent inhomogeneity of the hyperfine induced STM.

From the temperature dependent values of $H_{1/2}$ the rate k_T can be determined to increase from 3ns^{-1} at 290K to 5ns^{-1} at 90K. This activationless behaviour of k_T is the same as that observed in bacterial RCs. The absolute values of k_T in PSII are only slightly larger than the values observed in bacterial RCs (0.5-1ns^{-1}). It can be concluded that the electronic coupling between P680 and Pheo in PSII is very similar to the coupling between the corresponding pigments in the bacterial RC. Since the electronic coupling depends exponentially on the distance between the interacting pigments, as well as on their orientation, these results suggest a close similarity between the structures of the two RCs.

From the lack of a magnetic field dependence of the lifetime of $^3P680^*$ (1ms), which shows that no significant thermal reactivation from $^3P680^*$ to $^3(P680^+Pheo^-)$ occurs, a lower limit for $\Delta G(P680^+Pheo^- - {}^3P680^*)$ of 0.22eV can be estimated. Similarly, the observed inverse temperature dependence of $H_{1/2}$ allows to estimate a limit for the thermal repopulation from $^1(P680^+Pheo^-)$ to $^1P680^*$, yielding a lower limit of $\Delta G({}^1P680^* - P680^+Pheo^-)$ of 0.12eV. Together with the well known energies of $^1P680^*$ and $^3P680^*$, it can be concluded that not only the structure, but also the energetics governing charge separation in PSII are very similar to those in the bacterial RC.

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POSTER 50

MAGNETIC FIELD EFFECTS IN THE PHOTOLYSIS OF 7-SILANORBORNADIENE

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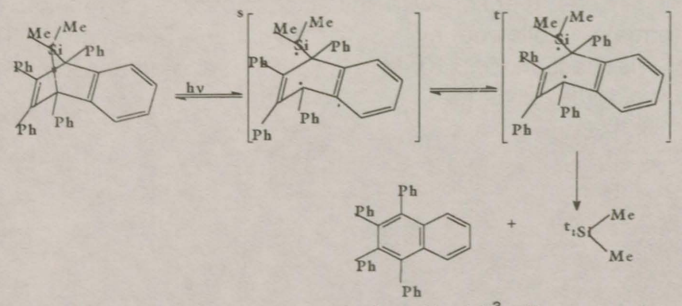
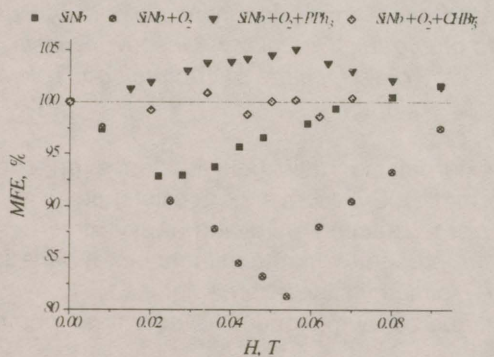
The observation of the external magnetic field influence on chemical reactions is the real proof of the S-T conversion existence. Though a number of MFE examples for the reaction, involving heavy atom centered radicals, is rather limited. In the present work the influence of magnetic field on photodecomposition of 7,7-dimethylsilanorbornadiene (**1**), known as a silylene precursor, has been studied by microsecond laser flash photolysys (XeCl, 308 nm).

From the CIDNP effects' analysis the intermediate formation of biradical has been assumed (Scheme 1). It gave us the possibility to expect the significant magnetic effect in this system.

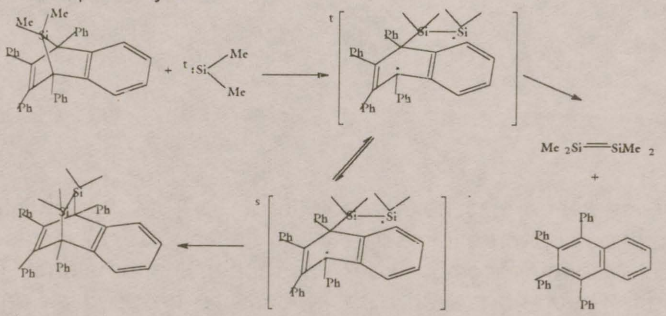


After irradiation of **1** hexane solution (1×10^{-3} M) we registered the stable absorption appeared immediately after laser pulse. It was ascribed to final product of photodecomposition -- tetraphenylnaphthalene (TPN). Its yield depends linearly on laser intensity and can be used as an internal standard. We have not succeeded to register the silylene itself, because of its short life-time. The presence of silylene quenchers, such as oxygen, bromoform and triphenylphosphine, is found to reduce the TPN yield. Moreover, the bromoform quenches the excited state of **1** according to Perrin equation, and the triphenylphosphine according to Stern-Volmer one ($k\tau = 2.2\times10^2$), that serves an indication of different quenching mechanisms.

The external magnetic field has no influence on kinetic curve shape, but reduces TPN yield. The magnetic field effect was expressed by the ratio of optical densities, monitored at 334 nm, in the presence and in the absence of magnetic field MFE = (D_H/D_0). Figure 1 demonstrates the observed magnetic field dependence of TPN yield on external magnetic field intensity. In the absence of any silylene quenchers the field dependence minimum is located around 0.022 T. It forces us to conclude that S-T conversion in biradical is due to exchange interaction (J). The observed MFE sign is opposite to that predicted by theory for singlet precursor.



Excitingly, the addition of silylene quenchers changes dramatically the shape of field dependence and MFE magnitude (Figure 1). Oxygen replaces the field dependence minimum to higher fields (0.055T), the addition of triphenylphosphine alters the sign of magnetic effect, and bromoform decreases it to zero. These facts force us to assume the existence of another magnetic sensitive stage, whose final product is also TPN. The subsequent silylene reaction with initial **1** is supposed to pass through biradical formation followed by S-T conversion (Scheme 2). The rate constant of this reaction (5.7×10^9 $M^{-1}c^{-1}$) could lead to an assumption on the participation of triplet silylene.



So the observed magnetic field effect is the superposition of effects, formed in these two biradicals. The quantum-chemical calculations support the necessity of two stages. The contribution of second biradical to "total" MFE is more significant than that one of first.

The more exhaustive explanation is now in progress.

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POSTER 51

THE SNP MEASUREMENT OF THE ELECTRON-TRANSFER REACTION BETWEEN QUADRICYCLANE AND TETRAFLUORO-*P*-BENZOQUINONE.

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In the electron-transfer reaction between quadricyclane (QC) and tetrafluoro-*p*-benzoquinone (TFBQ), norbornadiene (NB) is created through the isomerization reaction from quadrycyclane cation radical $(QC^{+\bullet})$ to norbornadiene cation radical $(NB^{+\bullet})$.[1]. In this report by using SNP (stimulated nuclear polarization) method, we examine whether the isomerization occurs in cage of radical-ion pair or in free radical.

SNP spectrum of QC and NB are shown in fig. 1 and fig. 2, where we monitor the protons of cyclobutane (fig. 1) and olefine (fig. 2) positions. From the E/A pattern of the SNP spectrum and the sign of the hyperfine coupling constant[2], we conclude that QC is the geminate recombination product. In view of the known[3] signs of the hyperfine coupling constant of cation radicals, $QC^{+\bullet}$ and $NB^{+\bullet}$, and the observed A/E pattern of the SNP spectrum may be interpreted in terms of the following mechanisms. (1) NB is the escaped product of radical-ion pair $\overline{QC^{+\bullet}\ TFBQ^{-\bullet}}$ and free cation radical isomerizes. (2) NB is the geminate recombination product of $\overline{NB^{+\bullet}\ TFBQ^{-\bullet}}$ and isomerization occurs in cage of radical-ion pair. The second mechanism is unlikely because the shape of SNP spectrum should be distorted by the modulation of hyperfine interaction in radical-ion pair. Therefore, we conclude that $NB^{+\bullet}$ radical is created from free $QC^{+\bullet}$ radical.

We also perform time-resolved SNP measurement. From the time profile of SNP which appears in QC, we estimate that cage lifetime of radical-ion pair is about 60 ns taking into account time constant of detection system.

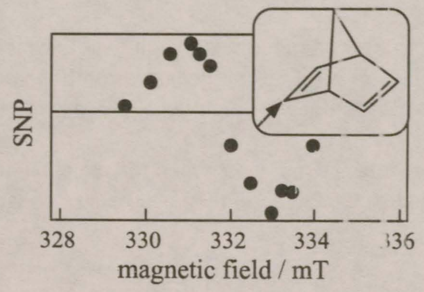

Figure 1: SNP spectrum of quadricyclane.

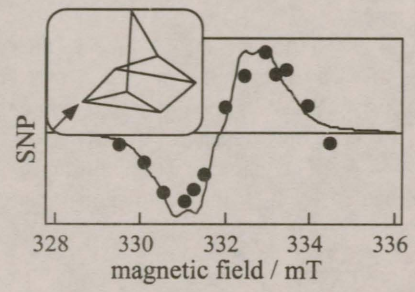

Figure 2: SNP spectrum of norbornadiene.

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POSTER 52

Flip-Flop Transitions and Micelle Size Effects on ESR spectra of Spin Correlated Radical Pairs.

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It was demonstrated [1], both theoretically and experimentally, that the rate of spin exchange relaxation governs the line shape and the value of APS splitting in TR ESR spectra of geminate micellized SC RP. Here we report the results of experimental observation of the effects of flip flop electron nuclear transitions on the line shape of TR ESR spectra of SC RP in micelles of different sizes.

The photodissociation (excimer laser, λ = 308 nm) of the triplet excited state of 2,4,6-trimethylbenzoyl diphenylphosphine oxide (TMDPO) results in the triplet geminate pair of diphenylphosphonyl and 2,4,6-trimethylbenzoyl radicals [2]. The micelle size was varied by the number of hydrocarbon atoms n = 8 - 12 in the hydrophilic tail of sodium alkylsulfate detergents.

At any delay time the time-resolved ESR spectra of RP consist of doublet of diphenylphosphonyl radical ($A[^{31}P]=38.3$ mT) and central line of 2,4,6-trimethylbenzoyl radical.

At short (< 100 ns) delay time both the low field ($M_s[^{31}P]=1/2$) and high field [$M_s[^{31}P]=-1/2$] lines of doublet are strongly TM polarized positively (A) in large (C_{12} and C_{11}) micelles. At intermediate (300 - 600 ns) delay time the low field ESR resonance transforms (Fig. 1) into antiphase (E/A, E = emission) pattern, with the high field line remains positively polarized. Finally, at long (> 1 μs) delay time the low field line transforms into totally emissive (Fig.1) one while the high field line just disappears from spectra.

In the small (C_8) micelles the APS pattern of both the low and high field lines is observed at even the shortest delay. The intensities of positive and negative components of low field APS are comparable, while the positive component of high field APS pattern far exceeds the intensity of negative one.

The value of APS splitting of low field resonance increases when the micellar size decreases. It is significant (Fig.1) that the dependence of APS on the micellar size consists predominantly of the shift of positively polarized line into high magnetic field, whereas the resonance frequency of negatively polarized line weakly depends on the micellar size.

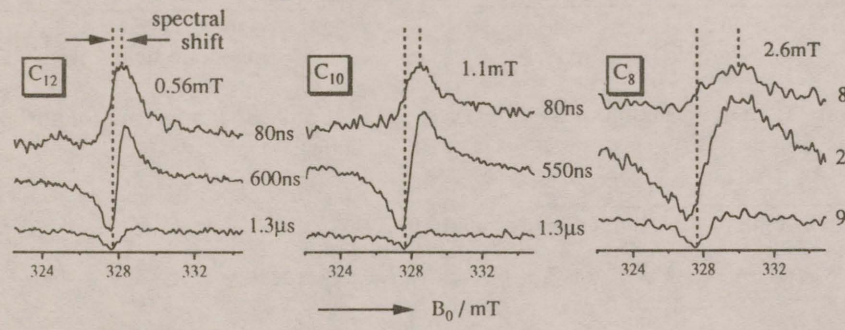

Fig.1 Time trasformation of low field resonance

There are four characteristic features which are most likely to have been taken into account to explain the time transformation of the spectra and their dependence on the micellar size. Firstly, despite of the strong value of hfc the motion of electron spins is predominantly nonadiabatic, thus, the populations of $\alpha_e\beta_e;\alpha_n$, $\alpha_e\beta_e;\beta_n$, $\beta_e\alpha_e.\alpha_n$, and $\beta_e\alpha_e.\beta_n$ electron nuclear spin levels are equal in magnitude. Secondly, $S\beta_n$-$T_-\alpha_n$ transitions in the vicinity of a crossing of corresponding spin levels result in fast equilibration between populations of $\beta_e\beta_e;\alpha_n$ and $\alpha_e\beta_e;\beta_n$ levels after nonreactive forced encounters and, in turn, lead to fast decreasing in intensity of low field "T" and high field "S" lines (transitions are symbolized in Fig. 2). Thirdly, at large distances between radicals, $T_+\beta_n$ - $S\alpha_n$ and $T_-\alpha_n$-$S\beta_n$ transitions itself do not lead to the variation in the populations of adiabatic levels, except that the chemical reaction decreases the population of the S-correlated levels. In consequence of this feature the population of $\alpha_e\alpha_e;\beta_n$ ($\beta_e\beta_e;\alpha_n$) levels becomes smaller than that of $\alpha_e\alpha_e;\alpha_n$ ($\beta_e\beta_e;\beta_n$). This creates ESR spectrum which is very similar to RPM (Fig. 3). The fast spin selective radical recombination effectively promotes to this mechanism. It is apparent that the decreasing in micelle size causes an increase in the rate of relaxation and rate of chemical reaction as well. Fourthly, the spectrum of SC RPM is formed at the distances between radicals where the intensity of exchange interaction is comparable with the hfc. Creating of emissive component of low field APS is dictated by a creation of the difference in population of the corresponding adiabatic spin levels which is caused by both the level crossing spin exchange relaxation and the spin selective chemical reaction. That is why the low field emissive resonance weakly depends on the micellar size. On the other hand, this experimental observation clearly indicates that the average exchange is of secondary importance to provide the value of APS.

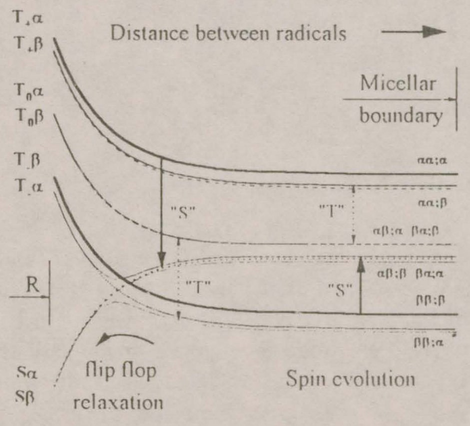

Fig.2 Final population of SC RP spin levels

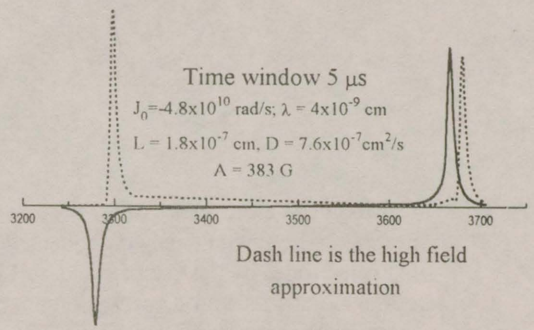

Fig.3 Illustration of the effect of flip flop transitions on TR ESR of SC RP

References:
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POSTER 53

MAGNETIC FIELD EFFECTS ON PHOTOELECTROCHEMICAL REACTION OF MODIFIED ELECTRODES WITH PORPHYRIN-VIOLOGEN LINKED COMPOUNDS

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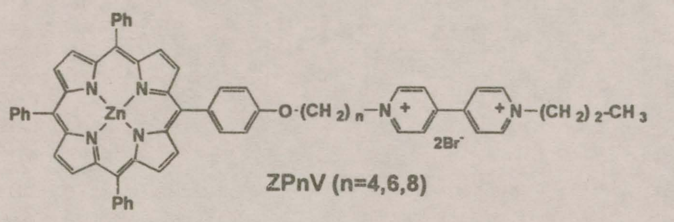
Donor(D)-acceptor(A) linked compounds in various organized molecular environments are expected to serve as a model system for studing the electron-transfer reactions in biochemical systems such as photosynthesis. The present authors have actually obtained photogenerated radical pairs of the linked compounds, and the lifetime of the radical pair was remarkably extended in the presence of magnetic field (MF).[1)] As a consequence, MF has been suggested as a novel means of controlling photoinduced electron-transfer and the succeeding processes.

In the present paper, as an application of the magnetic field effects (MFEs), we attempted to observe MFEs on photoelectrochemical reaction of modified electrodes with D-A linked compounds as Langmuir-Blodgett (LB) films.



ZPnV (n=4,6,8)

Modified electrodes were prepared by depositing the mixed monolayer with porphyrin-viologen linked compounds (**ZPnV**: n=4,6,and 8) and arachidic acid (1:10) on ITO electrodes by the use of standard LB method. A three electrode cell, which consists of the modified electrode as working, an Ag/AgCl electrode as reference, and a platinum electrode as counter, was used. The photocurrents of the modified electrode were measured under a controlled potential at 0 V vs Ag/AgCl in the presence of triethanolamine (10 mM) as a sacrificial electron donor under nitrogen atmosphere.

Photoirradiation with visible light (>400 nm) upon the modified electrode of **ZP8V** afforded stable anodic photocurrents (Fig. 1). The action spectrum of the modified electrode was in good agreement with the absorption spectrum of the porphyrin moiety of **ZP8V** in LB films. The result strongly indicate that the photocurrents were attributable to the excitation of the porphyrin moiety.

In the presence of MF, the photocurrent was clearly increased (Fig. 1). The increment of the photocurrent increased with MF and became constant value (ca. 15%) at above 0.3 T as shown in Fig. 2. The MFEs on the photocurrents were in good agreement with those on the lifetime of radical radical pairs in the same compounds.[2)] The same MFEs were observed, when the direction of MF was reversed. As a reference system, another modified electrode was prepared by using the porphyrin derivative without viologen moiety. Photocurrents were similarly obtained, although no magnetic field effects were observed. These results indicate that the MFEs do not come from magnetohydrodynamic effects, but are explained in terms of radical pair mechanism. Essentially the same phenomena were also observed with **ZPnV** (n=4 and 6). The magnitude of MFEs on the photocurrents with **ZP4V** was smaller than those with **ZP6V** and **ZP8V**. The results are consistent with those in our previous paper.[2)]

On the basis of these observations, the photocurrents were mainly ascribed to photoactive triplet radical pairs as generated by intramolecular electron transfer process in porphyrin-viologen linked compounds at the electrode surface. In addition, the MFEs on the photocurrents was explained by retardation of radical decay process via intersystem crossing.

Finally we have observed, for the first time, the MFEs on the photoelectrochemical reaction of the modified electrodes. The discovery will lead to an epochmaking means of reaction control involving electrochemical processes in LB films and the related systems.

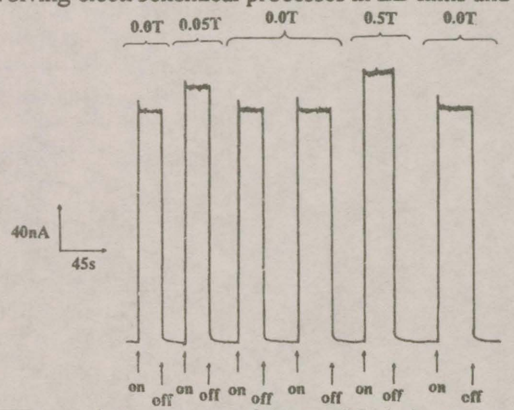


Fig. 1. MFEs on photocurrents of the modified electrode with **ZP8V**.

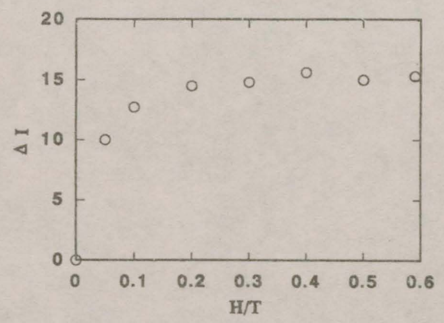


Fig. 2. Magnetic field effects on the fractional increment ($\Delta I = (I(H)-I(0))/I(0) \times 100$) of photocurrent of modified electrode with **ZP8V**. The photocurrent in the presence and absence of magnetic fileds is denoted by I(H) and I(0), respectively.

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