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Spin and Molecular Dynamics in Acyl-Containing Biradicals: Time-Resolved Electron Paramagnetic Resonance and Laser Flash Photolysis Study

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A combination of time-resolved electron paramagnetic resonance (TREPR) and laser flash photolysis (LFP) studies of flexible acyl-containing biradicals over a wide temperature range is reported. In contrast to previous reports, it is shown that the main channel of intersystem crossing in these biradicals is the electron spin relaxation of the acyl moiety rather than spin−orbit interaction in the biradical. This relaxation determines the decay rate of the electron spin polarization at low temperatures and the biradical lifetime at high temperatures. The relaxation mechanism is attributed to the spin-rotation interaction, associated with the rotation of the carbonyl group about the neighboring C−C bond axis. From a model simulation of the time profile of the spin-polarized TREPR signal based on the numerical solution of the stochastic Liouville equation of the spin density matrix in frame of realistic model of biradical, the Arrhenius parameters for correlation times of spin rotation interaction and activation energies for molecular and spin dynamics were determined in two solvents, 2-propanol and hexane.

Introduction

Flexible biradicals in which a polymethylene chain links the radical centers are good models for long-lived radical pairs with restricted mobility. Many such structures show strong magnetic field and spin effects and have been extensively studied over the last two decades.[1−9] It has been established that these effects result from the complex interplay of spin and molecular dynamics. In particular, the dynamics of the polymethylene chain changes the inter-radical distance from an extended to a closed conformation, whereas the spin dynamics are responsible for the transitions between triplet and singlet (reactive) states of a biradical. Formed initially in the triplet electronic state from an excited triplet state precursor molecule, biradicals undergo intersystem crossing (ISC) to a reactive singlet state from which they can react if the distance between the radical centers is sufficiently small. The molecular dynamics of the polymethylene chain modulate the exchange interaction, which affects the efficiency of singlet−triplet transitions in biradicals. These transitions are governed by different magnetic interactions (Zeeman interaction, hyperfine interaction, and relaxation), as shown in Scheme 1. It has been demonstrated that for many biradicals at room temperature in nonviscous solvents the molecular dynamics ("horizontal" transitions in Scheme 1) are much faster than the spin dynamics ("vertical" transitions) and ISC is the rate determining step for the biradical lifetime.[9,10] Since the rate of ISC depends on the external magnetic field, a very strong influence of the magnetic field on biradical lifetime is often observed.[7,8,11−13]

In this respect, biradicals containing an acyl radical fragment are an exception. They demonstrate only weak magnetic field effects,[6,8,14] and even in the absence of an external magnetic field their lifetimes are much shorter[6,14,15] than the lifetimes of nonacyl biradicals of similar size (such as bisbenzyl,[12] bisketyl,[8] or ketyl−alkyl[11] biradicals). It has been commonly accepted that the anomalous behavior of acyl-containing biradicals is accounted for by spin−orbit coupling (SOC) in the two-spin system, which, at short distances between radical centers and favorable mutual orientations of electron orbits, causes recombination of triplet biradicals.[1,10,14,16−19] This phenomenon, called intersystem recombination (ISR), has been studied theoretically[20−24] and for short biradicals this phenomenon has been

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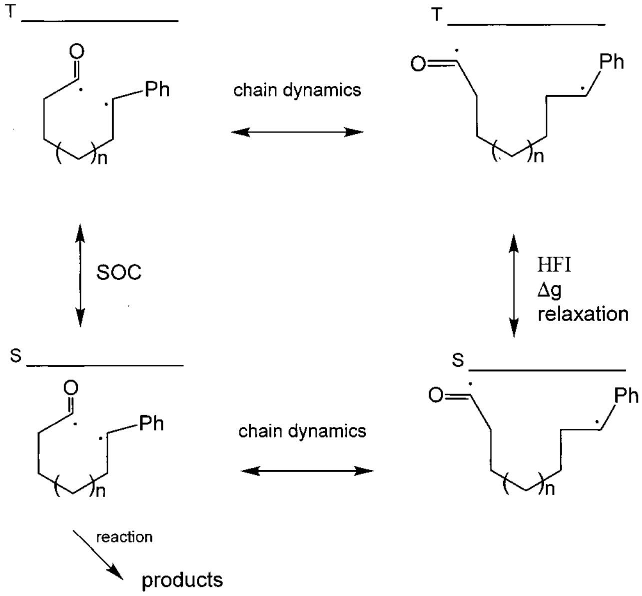

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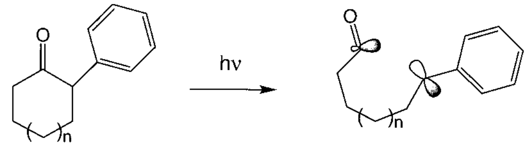
SCHEME 2



1: n = 9 **1a**
2: n = 5 **2a**

confirmed by the experiments of de Kanter and Kaptein.[25] The ISR process does not depend on the magnetic field; incorporation of the corresponding terms into equations for spin and molecular dynamics in biradicals allows for a good quantitative description of most of the experimental results obtained to date.[1,8,10,15,26−28]

Another possible source of fast magnetic field-independent ISC in acyl-containing biradicals can be a longitudinal electron spin relaxation of the acyl moiety. This possibility has been ruled out by Turro[29] on the basis that the rate of ISC in such biradicals decreases with decreasing temperature, while for relaxation the opposite temperature dependence is typical. This could, for example, be due to a C−C−O bending vibration, which mixes states of different hybridization at the radical carbon. In fact, there is a sparse dataset on relaxation rates and mechanisms of acyl radicals in the literature. The most quantitatively reliable measurements date to 1975, when Paul studied the relaxation of the formyl radical,[30] where it was shown that the relaxation time of H$\dot{C}$O increases with decreasing temperature. It was proposed that the main mechanism of relaxation is spin-rotational interaction caused by a large spin-rotational coupling along the C═O bond. If this mechanism of spin relaxation remains effective for acyl radicals larger than formyl, it can be responsible for the fast ISC in acyl-containing biradicals. The essential difference between ISR and electron spin relaxation is that ISR is effective only at a short distance between the radical centers, while spin relaxation can cause triplet−singlet interconversion at any inter-radical distance. It is possible to discriminate between the two mechanisms, ISR or electron spin relaxation of the acyl moiety by comparison of the temperature and viscosity dependences of both the lifetime and of the electron spin relaxation rates in acyl biradicals.

In this paper, we present the results of kinetic measurements of chemically induced electron spin polarization (CIDEP) and the transient optical absorption of a 1,16 acyl−phenyl biradical detected under closely matched experimental conditions. Most of the experiments have been conducted with acyl−benzyl biradical **1a** (Scheme 2) formed under UV irradiation of 1-phenylcyclotetradecanone, **1**. The model simulations of the time profiles of the CIDEP signal were carried out using a realistic model for flexible biradicals. The main goal of this study is to investigate the temperature and viscosity dependences of molecular and spin dynamics in flexible acyl-containing biradicals in order to distinguish which of the two mechanisms, ISR or relaxation of the acyl moiety, is responsible for the fast magnetic field-independent ISC.

Experimental Section

Our TREPR apparatus has been described elsewhere.[27,31] The measurements were performed on a JEOL, USA Inc. (Peabody, MA) JES RE-1X X-band (9.46 GHz) EPR spectrometer. The solutions, flowing through a cylindrical cell placed inside a dewar, were irradiated with pulsed light from a Lambda Physik LPX-100i excimer laser operating at 308 nm (XeCl). The solution temperature was measured using a thermocouple placed inside the cell just above the irradiated volume. While there is a temperature gradient of several degrees between the entrance and exit of the flow system, there is no measurable gradient between the irradiated part of the sample and the thermocouple as they are less than a millimeter apart.

The temperature-independent response time of the resonator (τ_r = 70 ns) was maintained by insertion of a capillary containing water into the resonator. The capillary remained outside the sample dewar (Q-spoiling). The resonator response time was taken into account during data treatment by a convolution of all calculated kinetics with the expression exp($-t/\tau_r$). All solutions were purged with nitrogen for 30 min prior to and during irradiation. For obtaining field-swept TREPR spectra, the output of the microwave bridge preamplifier was fed to the input of a Stanford Research Systems (SRS) boxcar signal averager SR 250 (Sunnyvale, CA), whereas for kinetic measurements a LeCroy 9400B (Spring Valley, NY) transient digitizer was used.

A detailed description of the laser flash photolysis (LFP) equipment has been published.[32,33] Solutions in a rectangular cell (10 mm × 10 mm) were irradiated with a Lambda Physik EMG 101 excimer laser (308 nm, pulse energy up to 100 mJ). The dimensions of the laser beam at the front of the cell were 3 mm × 8 mm. The monitoring system includes a DKSh-120 xenon short-arc lamp connected to a high-current pulser, two synchronously operating monochromators, a Hamamatsu R955 photomultiplier, and a LeCroy 9310A digitizer. All solutions were purged with argon for 15 min prior to and during irradiation. Typical initial biradical concentrations were $\sim 10^{-5}$ M in all experiments.

The compounds 1-phenylcyclotetradecanone, 1,12-dimethyl-1-hydroxycyclododecanone, and 2,2,10,10-tetramethyycyclodecanone were synthesized as described in the literature.[34] The purity of the reagents was >98% by ^{1}H NMR spectroscopy and GC/MS.

Results

A. Laser Flash Photolysis (LFP) Measurements. The transient absorption kinetics of the decay of biradical **1a** was measured at 260 nm, the absorption maximum of benzyl radical.[35−37] Measurements were performed in two solvents, 2-propanol and hexane, at temperatures ranging from 191 to 294 K. The kinetics of the signal decay did not depend on laser power, and at each temperature the data fit well to an exponential function in both solvents. Representative kinetic traces are shown in Figure 1, and Figure 2 shows the temperature dependence of the first-order rate constant of the biradical decay. At temperatures above 240 K the rate constants of the biradical decay in 2-propanol and hexane coincide, even though the viscosities of two solvents at 240 K differ by a factor of 30 (17 cP for 2-propanol and 0.56 cP for hexane).[38] Therefore, in the high-temperature region, the molecular dynamics of the biradical are faster than ISC, and the biradical lifetime is determined by the rate of viscosity-independent triplet−singlet conversion.

Below 240 K the temperature dependences in two solvents are separated: biradical decay in 2-propanol becomes significantly slower than that in hexane. Thus, for **1a** the temperature 240 K is a crossing point from a region of fast conformational movement to a region where molecular dynamics is slower than the spin wave function evolution. It should be noted that even at very low temperatures, where the biradical lifetime is determined exclusively by the rate of the conformational

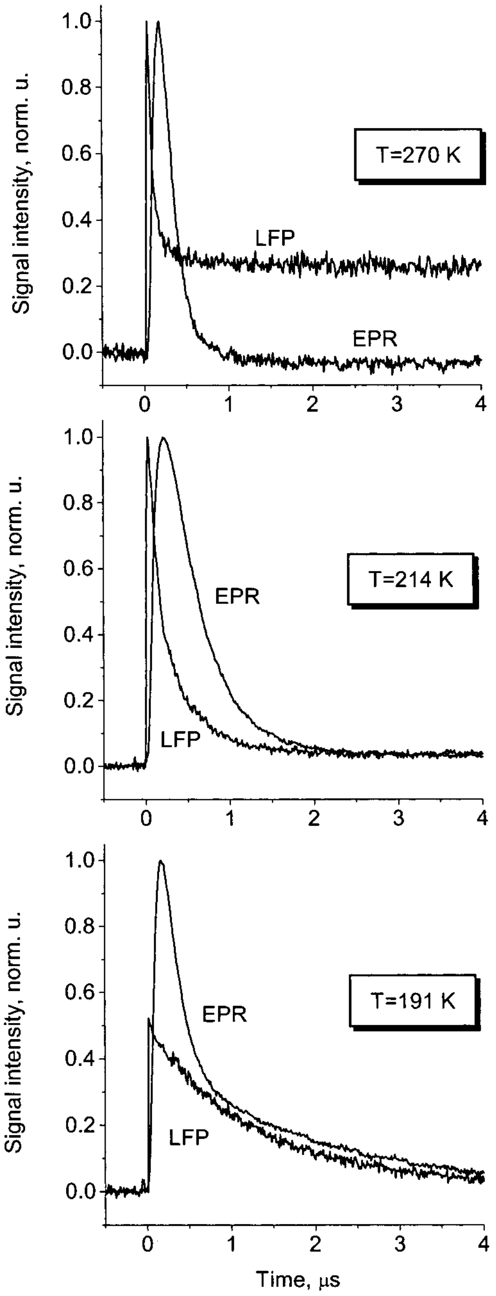


Figure 1. Transient absorption kinetics and time profiles of SCRP polarization of acyl−phenyl biradical **1a**, recorded at different temperatures in 2-propanol.

movement (or, in terms of Scheme 1, by the rate of transition from the extended to the closed state of the biradical), the biradical lifetime is not proportional to the solvent viscosity. For example, at 190 K the decay rate constants for **1a** in 2-propanol and hexane are 4.5×10^5 and 2×10^6 s^{-1}, respectively, whereas the viscosities differ by more than 2 orders of magnitude (300 cP for 2-propanol and 1.4 cP for hexane).[38] Therefore, the rate of the conformational movement of polymethylene chain is not proportional to the diffusion coefficient. For this reason the motion should be treated as a thermally activated process. Indeed, Arrhenius plots for the rate constant of biradical decay in the low-temperature region (Figure 3) show a good linear relationship. The activation energies derived from the plot are 21.9 ± 1.7 kJ/mol for 2-propanol and 15.1 ± 1.4 kJ/mol for hexane.

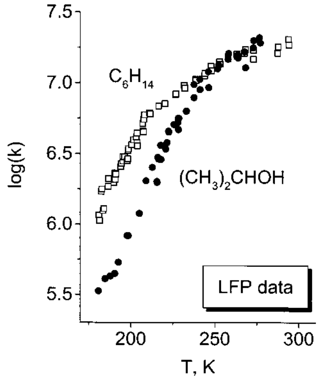


Figure 2. Temperature dependences of the decay rate of **1a** in 2-propanol (●) and hexane (□).

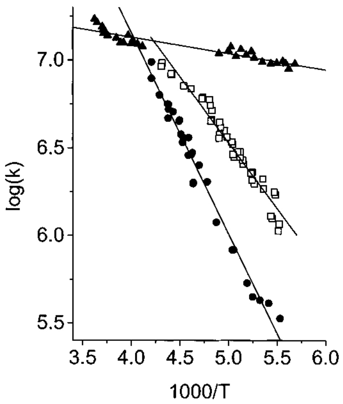


Figure 3. Arrhenius plots for the low-temperature part of the temperature dependence of the decay rate of **1a** in 2-propanol (●) and hexane (□) and for the decay of polarization ("horizontal" branch in Figure 6) (▲).

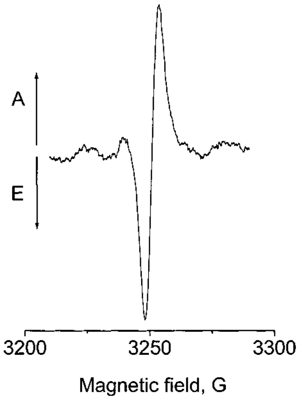


Figure 4. TREPR spectrum of acyl−phenyl biradical **1a**, obtained at 300 ns after a 308 nm laser flash at 205 K in 2-propanol.

A similar temperature dependence (not shown) was obtained for the 1,12-acyl−ketyl biradical formed under irradiation of 1,12-dimethyl-1-hydroxycyclododecanone in 2-propanol. The activation energy obtained in the low-temperature region for this structure was 22.2 ± 1.5 kJ/mol.

B. Time-Resolved Electron Paramagnetic Resonance Measurements. Figure 4 shows the TREPR spectrum of acyl−benzyl biradical **1a.** It consists of two broad intense positive and negative components whose centers are separated by approximately 7 G, accompanied by much weaker sidebands. The observed electron spin polarization pattern is due to the spin correlated radical pair (SCRP) mechanism, well-known for biradicals[6,27,39] and radical pairs in micelles[40] or in viscous solutions.[41] The symmetry of the spectrum indicates that with 13 C−C bonds between the radical centers, S−T^- mixing does not make a significant contribution to the spin wave function evolution of the biradical. We therefore conclude that the main mechanism of polarization formation is S$-$T^0 mixing. The shape of the spectrum does not change noticeably with time. With decreasing temperature, the signals become somewhat narrower, and the minima and maxima shift their magnetic field positions slightly. These spectral transformations are explained by changes in the amount of spectral exchange broadening and resonance shifts of the antiphase structure. This phenomenon is commonly observed in the temperature dependence of SCRPs[42] and does not affect these results as all kinetic measurements were carried out at the maximum (or minimum) at any given temperature.

The kinetics of the absorptive maximum of TREPR signal, obtained after the laser irradiation of 4 mM of **1** in 2-propanol at different temperatures, are shown in Figure 1. The minimum of the emissive component of the SCRP spectrum shows a similar time evolution at each temperature. The shapes of the kinetic curves do not change with a variation of the microwave power from 0.1 to 5 mW over the entire temperature range studied. No changes were detected with the variation of the laser pulse energy or with the initial concentration of precursor **1**. Thus, we can presume that bimolecular interactions of biradicals (Heisenberg exchange and bimolecular reactions) do not influence the EPR kinetics, and a solution of the Bloch equations for the time evolution of EPR-detected magnetization is given by[43]

$$v(t) = A\exp(-\sigma_0 t)\sin(\omega_T t) \tag{1}$$

with

$$\sigma_0 = 0.5(1/T_1 + 1/T_2) \tag{2}$$

and

$$\omega_T = \sqrt{[(B_1{}^2 - 0.25(1/T_1 - 1/T_2)^2]} \tag{3}$$

Here A is a time-independent constant, B_1 is the microwave field, and T_1 and T_2 are the longitudinal and transverse relaxation times. Since the kinetics of the TREPR signals shown in Figure 1 do not depend on the amplitude of B_1, the condition $B_1 \ll 1/T_1$, $1/T_2$ is always met in these experiments. Thus, the function $\sin(\omega_T t)$ in eq 1 can be replaced with the linear function t. Additionally, we can assume that $1/T_1 = 1/T_2$, and for notation we use the rate constant k_1 for $1/T_1$. In this case, eq 1 becomes

$$v(t) = Bt\exp(-k_1 t) \tag{4}$$

where B is a normalization constant.

The kinetics of the TREPR signal in the high-temperature region in 2-propanol (210$-$280 K) are well described by eq 4. For kinetic traces obtained in hexane, a good fit to eq 4 was obtained for all temperatures. The values of the rate constant k_1 gradually decrease with temperature. The temperature dependence of k_1 in hexane is shown in Figure 5 together with the corresponding results of the LFP measurements.

In 2-propanol at temperatures below 210 K it becomes apparent that the kinetic trace of the TREPR signal contains two components, one fast and one slow (Figure 1, trace labeled 191 K). With further temperature decreases, the decay rate of the fast component changes only slightly, whereas the slow component becomes significantly slower and its initial amplitude decreases. At very low temperatures (below 190 K) the slow component becomes practically flat, and the major polarization decay again becomes monoexponential. Thus, a drastic difference between the decay of transient absorption signal and the decay of TREPR signal was observed at low temperatures: the biradical lifetime extends to microseconds, while the rate constant for spin polarization decay is of the order of 10^7 s^{-1}.

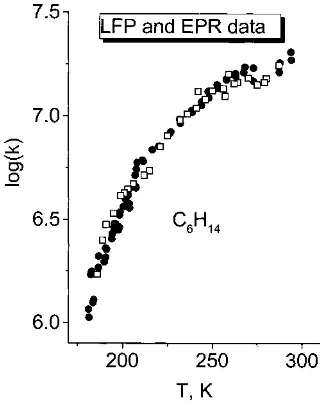


Figure 5. Temperature dependences of the decay of SCRP polarization of **1a** (□) and of the decay of the optical absorption of **1a** (●) in hexane.

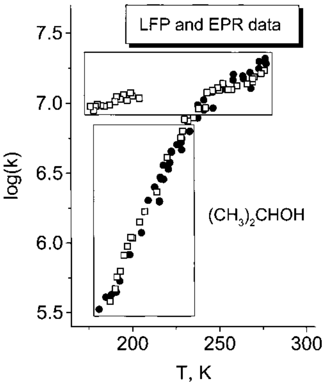


Figure 6. Temperature dependences of the decay of SCRP polarization of **1a** (□) and of the decay of optical absorption of **1a** (●) in 2-propanol.

The traces obtained above 210 K and below 190 K were fitted to eq 4, whereas the kinetics in the intermediate region (190$-$210 K) were treated as a sum of eq 4 and a convolution of eq 4 with the function $\exp(-k_2 t)$:

$$v(t) = B_1 t\exp(-k_1 t) + B_2\int_0^t [y\exp(-k_1 t)\exp(-k_2(t-y))]\,\mathrm{d}y \tag{5}$$

Thus, in Figure 6 two rate constants (k_1 and k_2) are presented for the temperature range between 190 and 210 K. The meaning of the two rate constants, k_1 and k_2, will be discussed below.

We have also performed the TREPR measurements of a shorter 1,10-biradical formed under irradiation of 2,2,10,10-tetramethylcyclodecanone. At room temperature the acyl$-$alkyl biradical undergoes decarbonylation with the rate constant $k_{-\mathrm{CO}} = 3 \times 10^5$ s^{-1},[44] and EPR spectra obtained at different delays after the laser pulse present a mixture of 1,10-acyl$-$alkyl and 1,9-bisalkyl biradicals.[6,27,39] At lower temperatures the decarbonylation rate constant significantly decreases,[37] and this reaction can be disregarded.

The TREPR spectrum of 1,10-acyl$-$alkyl biradical (**2a**) has been published earlier.[6,27,39] Unlike **1a**, the spectrum of **2a** is asymmetrical, with predominance of emission over absorption. This asymmetry is attributed to the contribution of S$-$T$^-$ mechanism of CIDEP formation, which is more pronounced for shorter biradicals.[6,27,39] Figure 7 shows the EPR kinetics of absorptive and emissive components of polarization, obtained at 183 K in 2-propanol and demonstrates the transformation of

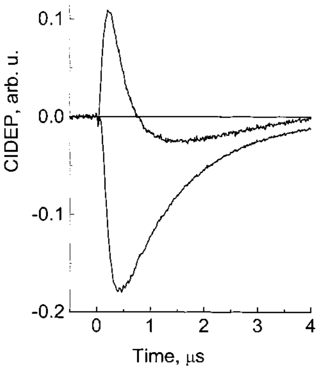


Figure 7. Kinetics of SCRP polarization of **2a** at 183 K in 2-propanol at two different field positions.

the EPR spectrum: at early times the spectrum represents an alternation of positive and negative components, typical for $S-T^0$ SCRP mechanism, whereas after 0.5 μs the spectrum becomes completely emissive due to the influence of the $S-T^-$ mechanism. It is important to note for future discussion that the decay rates of the positive component for **1a** and **2a** at the same temperature are very similar.

Discussion

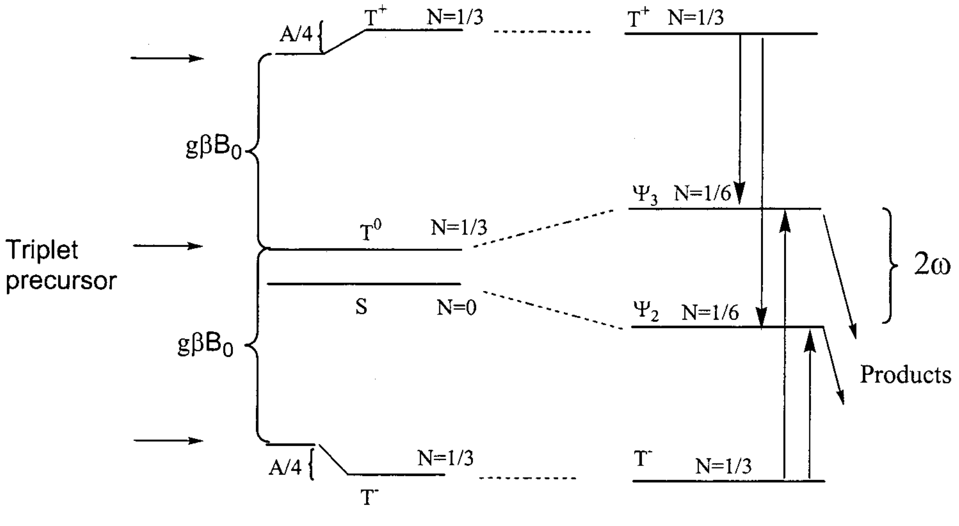
CIDEP formation in flexible biradicals by the SCRP mechanism has been considered earlier (Scheme 3).[6,27,39,40] Norrish type I photocleavage of the starting ketone results in formation of a biradical in a triplet "closed" state (see Scheme 1) with equal populations of the three high-field triplet states T^0, T^+, and T^-. As the radical centers separate, efficient $S-T^0$ mixing redistributes the population of the T^0 state between the two new spin states, ψ_1 and ψ_2, which are linear combinations of the T^0 and S states. The populations of the T^+ and T^- states become much greater than the populations of the ψ_1 and ψ_2 states, and this manifests itself as strong SCRP electron spin polarization.[6] The formation of this *primary* polarization occurs within a few nanoseconds and can therefore be considered to be instantaneous.[6] At later times, the radical centers again come close together, which leads to further depopulation of the ψ_1 and ψ_2 states due to chemical reaction from the singlet state, and a *secondary* electron spin polarization is formed. At room temperature, the transitions between the extended and close states proceed in subnanosecond time scale, and this process determines the rate of the secondary polarization formation. The rate of the polarization decay, as well as the biradical lifetime, is determined by the rate of the depopulation of the T^+ and T^- states. This decay can occur by three channels: ISR, electron spin relaxation, and hyperfine-induced $S-T^+$ and $S-T^-$ mixing. The latter can be ruled out for acyl-containing biradicals, since the lifetimes of these biradicals do not show significant magnetic field dependence.[6,8,14]

At low temperatures in viscous solvents (like 2-propanol) the molecular dynamics of the biradical become very slow, and the rate of the secondary polarization formation is much smaller than the rate of the primary polarization decay. This explains the appearance of two components in the TREPR kinetics in 2-propanol for the temperature range 190 K to 210 K: the fast component (k_1) corresponds to the decay of the primary polarization, whereas the slow component (k_2) shows the formation of the secondary polarization. At temperatures below 190 K the secondary polarization becomes too weak to be detected, whereas at temperatures above 210 K, evolution of the primary and secondary polarizations takes place on a comparable time scale and therefore they cannot be distinguished. The fact that the temperature dependence of the slow component practically coincides with the temperature dependence of biradical lifetime measured by LFP (Figure 6) is strong support for this assignment. Qualitatively, the kinetics of the secondary polarization formation in the region of slow molecular dynamics can be described in the following way: during the time when the biradical termini are apart, spin relaxation equalizes the populations of four levels ψ_1, ψ_2, T^+, and T^- (Scheme 3) with the rate constant k_1. When the biradical comes into the close conformation (rate constant k_2), the reaction takes place from the singlet state (approximately one-fourth of the total population). After separation of the biradical termini, the populations of ψ_1 and ψ_2 become much smaller than the populations of the T^+ and T^- states. This polarization decays due to relaxation, and so on. As a result, z-magnetization grows in with the fastest rate constant k_1 and decays with the slowest rate constant k_2:

$$M_z \sim \frac{k_2}{k_1 + k_2}(\exp(-k_2 t) - \exp(-k_1 t)) \qquad (6)$$

Thus, in the low-temperature region the observed rate constant for the secondary polarization formation, as well as the rate constant of biradical decay measured by LFP, is in fact the frequency of reencounters of the radical centers.

SCHEME 3



The only possible source of the decay is the uncorrelated electron spin relaxation of radical centers. Since the relaxation time of the benzyl radical lies in microsecond scale,[45] this fast relaxation should be attributed to the acyl radical center. Inspection of Figure 6 shows that the observed temperature dependence consists of two branches, marked by rectangles: the "vertical" branch corresponds to the molecular dynamics of the polymethylene chain, and the "horizontal" branch shows the temperature dependence of ISC in the biradical. A good correlation between low-temperature and high-temperature parts of the "horizontal" branch is strong evidence that in both temperature regions the same mechanism of ISC is effective, namely the relaxation of the acyl radical center. In the nonviscous solvent hexane the temporal separation of molecular and spin dynamics is not achieved even at temperatures near the freezing point (~178 K) of hexane (Figure 5).

Figure 3 demonstrates the Arrhenius plots for molecular dynamics of 1,14-acyl−benzyl biradical in hexane (low-temperature part in Figure 5), in 2-propanol (the "vertical" branch of Figure 6), and for ISC in 2-propanol (the "horizontal" branch of Figure 6). The activation energies obtained for the molecular dynamics are $E_{a1} = 21.9 \pm 1.7$ kJ/mol in 2-propanol and $E_{a2} = 15.1 \pm 1.4$ kJ/mol in hexane. Similar activation energies have been reported earlier for the conversion from extended to closed biradical conformations.[10,46,47] The higher activation energy in the viscous solvent 2-propanol is accounted for as the result of frictional forces exerted by the solvent.[48−50] For spin dynamics a value of $E_{a3} = 1.8 \pm 1.2$ kJ/mol was obtained.

Generally speaking, the fast relaxation of the acyl radical center can be attributed to several mechanisms: anisotropy of the **g**-tensor and/or the hyperfine tensor, spin-rotation interaction, or spin exchange interaction. The last can be ruled out since the polarization decay does not depend on the initial biradical concentration. Relaxation caused by **g**-tensor anisotropy strongly depends on the applied magnetic field, whereas the lifetimes of acyl-containing biradicals show only weak magnetic field dependence.[6,8,14] Also, in the fast-motion limit the rate of the relaxation caused by the anisotropy of **g**-tensor and HFI tensor should decrease with increasing temperature and decreasing solvent viscosity.[51] Experimentally (Figures 3, 5, and 6) the observed relaxation rate does not depend on the solvent viscosity and slightly increases with increasing temperature. Thus, the spin-rotation interaction is the only possible mechanism of electron spin relaxation of the acyl moiety.

Spin-rotation relaxation arises from the interaction of the electron spin with magnetic fields generated by the rotation of a molecular magnetic moment modulated by molecular collisions, and its rate can be expressed as

$$\frac{1}{T_1} = \frac{2kT}{3\hbar^2} C_{\mathrm{eff}}{}^2 I_{\mathrm{i}} \tau_J \tag{7}$$

where C_{eff} is the effective spin-rotational coupling constant, I_{i} is the moment of inertia of the molecule, and τ_J is the angular momentum correlation time.[52] The latter is often described as a function of viscosity η by a modified Stokes−Einstein relation[53]

$$\tau_J = I_i / 8\pi a_0{}^2 k\eta \tag{8}$$

where a_0 is the hydrodynamic radius of the molecule, and $0 < k < 1$ is a temperature and viscosity independent parameter. According to eqs 7 and 8 the spin-rotation relaxation rate should depend strongly on the solvent viscosity and the molecular size, which is clearly in contradiction with the experimental results. Therefore, we propose that the observed relaxation originates not from the molecular rotation modulated by collisions with solvent molecules but from the intermolecular rotation of C═O group about the neighboring C−C bond axis (propeller-like rotation) modulated by the fluctuation of molecular energy between internal vibronic and rotational states. The rotation of the small carbonyl group should be viscosity independent, and the angular momentum correlation time τ_J can be expressed in the form[54]

$$\tau_J = \tau_0 \exp(-E_r/RT) \tag{9}$$

We have to note that the "exponential" approach for the description of molecular and spin dynamics presented above is oversimplified. The main disadvantage of this approach is the presumption that in the temperature dependences the molecular and spin dynamics are separated: in the low-temperature region the biradical lifetime is determined by the molecular dynamics only, whereas in the high-temperature region it mainly depends on spin dynamics. In fact, the spin dynamics depend on the conformational movement of the biradical at any temperature, because the molecular dynamics vary the distance between the radical centers, modulate the exchange interactions $J(r)$, and consequently, affect the singlet−triplet conversion and thus the spin dynamics of biradicals. As a result, spin and molecular dynamics in biradicals are coupled together, which makes the separation of these processes useful for a qualitative explanation only. It is probably too rough an approximation for the quantitative description of the temperature dependences of the SCRP polarization and the transient absorption kinetics.

The most realistic model of molecular and spin dynamics in biradicals is based on the approach developed by de Kanter for a description of the CIDNP field dependences in the geminate recombination of biradicals.[55] The approach involves the numerical solution of the stochastic Liouville equation (SLE) for the spin density matrix ρ of a biradical. Earlier we have successfully used this approach for the calculation of spin and magnetic field effects observed in geminate evolution of short-lived flexible biradicals: CIDNP kinetics in a high magnetic field, CIDNP field dependencies, CIDEP spectra and kinetics, magnetic field effect on the biradical lifetime, stimulated nuclear polarization spectra, and kinetics.[8,9,15,28,44] According to this approach, the end-to-end distance distribution function of the biradical is divided into segments of equal area with an average distance r_i for each segment i. Transitions between neighboring segments i and k were described by the matrix elements $W_{ik} = W_{ki} = D/(r_i - r_k)^2$ with the effective diffusion coefficient D. Time evolution of the density matrix elements at r_i is determined by the following operators: Liouville operator, associated with the Hamiltonian, relaxation matrix, and the matrix describing chemical reactions.

The spin Hamiltonian includes the Zeeman interaction of the electrons having g factors g_1 and g_2 with the external magnetic field B_0, the secular part of the electron hyperfine interaction with one magnetic nucleus (hyperfine coupling constant A), the standard expression for the exchange interaction between the unpaired electrons $J(r) = J_0 \exp(-\lambda(r - r_0))$, and the interaction of the electron spin with the microwave field with frequency ω_1 and amplitude B_1. In the rotating frame of reference, the

Hamiltonian becomes time-independent and can be written as follows:

$$\hat{H} = \beta_e B_0 \hbar^{-1}(g_1\hat{S}_{1z} + g_2\hat{S}_{2z}) - \omega_1(S_{1z} + S_{2z} + I_z) + A\hat{S}_{1z}\hat{I}_z - J(r)(^1/_2 + 2\hat{\vec{S}}_1\hat{\vec{S}}_2) + \beta_e B_1 \hbar^{-1}(g_1\hat{S}_{1x} + g_2\hat{S}_{2x}) \quad (10)$$

The relaxation matrix contains elements arising from two mechanisms of spin relaxation: (a) uncorrelated relaxation, corresponding to the independent relaxation of the biradical termini and characterized by fluctuations of the local magnetic fields $G = \langle|B_i|^2\rangle$ and correlation time τ_u, and (b) correlated interactions, associated with the dipole−dipole interaction between unpaired electrons and characterized by rotational correlation time τ_c.

Chemical reactions were taken into account as recombination from singlet state with the rate constant k_r at the minimal r_i. We assume that the photolysis of starting ketones produces biradicals having equally populated triplet sublevels and at the minimal r_i at $t = 0$. In contrast to our previous model simulations of spin and molecular dynamics,[8,9,15,44] the spin−orbit interaction *is not included* in the SLE.

Four wave functions, S, T^0, T^+, and T^-, were used as a basis, and the spin density matrix consisted of 16 elements for each of 200 slices of the end-to-end distribution function. To calculate the time dependencies of TREPR line intensity $\langle\hat{S}_y\rangle$ at a magnetic field B_0, we solved the stochastic Liouville equation for the Fourier transform of the density matrix $\tilde{\rho}(\omega) = \int_0^\infty \rho(t)e^{-i\omega t}\,dt$. The resulting stationary equation for $\tilde{\rho}(\omega)$ could be solved numerically. The Fourier reconstruction of $\tilde{\rho}(\omega)$ yields a time-dependent density matrix $\rho(t)$, which allows us to obtain the TREPR kinetics according to the equation

$$\langle\hat{S}_y\rangle = \sum_j \langle\hat{S}_y\rangle_j = \sum_j \mathrm{Tr}[\hat{S}_y\rho_j] \quad (11)$$

where *j* denotes the number of a particular segment of the end-to-end distribution function. During the calculations the number of harmonics in the Fourier series was $n = 500$ with the highest frequency $\omega_0 = 2\pi n/T$ with $T = 5$ μs.

Three parameters, τ_u, τ_c, and *D*, were considered to be temperature dependent. For simulation of the temperature dependence of these observables we presumed that the effective diffusion coefficient *D* and the correlation time τ_u depend on temperature exponentially:

$$D = D_0 \exp\left(-\frac{E_D}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right)$$

and

$$\tau_u = \tau_{u0} \exp\left(-\frac{E_u}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right)$$

whereas for the correlation time τ_c the dependence

$$\tau_c = \tau_{c0}\frac{T_0}{T} \exp\left(-\frac{E_c}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right)$$

was used, with $T_0 = 273$ K. The energetic barrier E_c was set equal to the activation energy of the solvent viscosity η (i.e., $\tau_c \sim \eta/T$): $E_c = 22$ kJ/mol for 2-propanol and $E_c = 7$ kJ/mol for hexane.[38]

The kinetic curves, shown in Figure 8, were obtained according to eq 11 with the following parameters: $J_0 = -10^9$ mT, $\lambda = 2.14$ Å^{-1}, $k_r = 10^{11}$ s^{-1}, $A = 2$ mT, $D_0 = 2.6 \times 10^{-5}$ cm^2 s^{-1}, $E_D = 34$ kJ/mol, $G\tau_{u0} = 4.5 \times 10^6$ s^{-1}, $E_u = 8.9$ kJ/mol, $\tau_{c0} = 2 \times 10^{-10}$ s, $E_c = 22$ kJ/mol. As shown in Figure 8, the calculated EPR kinetics are in very good agreement with the experimental data. Similar results have been obtained for the kinetic data in hexane, with the same set of parameters except that $E_D = 23$ kJ/mol and $E_c = 7$ kJ/mol. The temperature dependences of the biradical lifetime, calculated with the same set of the parameters, are in a reasonably good agreement with the experimental data for both solvents. It is noteworthy that the energetic parameters obtained within this model are significantly higher than the activation energies extracted from the simple “exponential” approach: compare $E_D = 34$ kJ/mol in 2-propanol and $E_{a1} = 21.9 \pm 1.7$ kJ/mol; $E_D = 23$ kJ/mol in hexane and $E_{a2} = 15.1 \pm 1.4$ kJ/mol; $E_u = 8.9$ kJ/mol and $E_{a3} = 1.8 \pm 1.2$ kJ/mol.

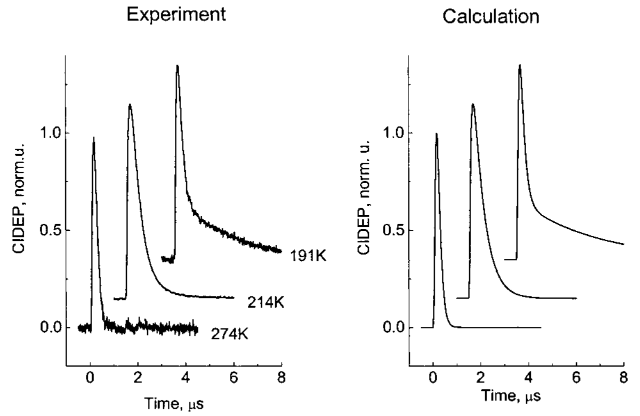


Figure 8. Experimental (left) and calculated (right) kinetics of SCRP polarization of **1a** at different temperatures. The calculation procedure and the parameters are given in the text.

The activation energies obtained for the effective diffusion coefficients *D* can be compared with the energetic barriers of transitions between three rotational conformations of the polymethylene chain, trans (tr) with a rotational angle $\phi_{tr} = 0°$, gauche+ (g^+) with $\phi_{g+} = 112°$, and gauche− (g^-) with $\phi_{g-} = 248°$: $\Delta E_{tr,g} = 14.6$ kJ/mol, $\Delta E_{g,tr} = 10.9$ kJ/mol, $\Delta E_{g,g} = 25.1$ kJ/mol.[56] The average value of three barriers is $\Delta E_{av} = 16.9$ kJ/mol. Addition to this value the activation energies of the solvents gives $\Delta E_{av} + E_c$(2-propanol) = 38.9 kJ/mol and $\Delta E_{av} + E_c$(hexane) = 23.9 kJ/mol, which agrees well with E_D values in two solvents.

The energy barrier for C=O rotation in the related compound acetaldehyde is ∼5 kJ/mol,[57] whereas in propionaldehyde it is ∼13 kJ/mol,[57] which is in good agreement with the activation energy $E_u = 8.9$ kJ/mol. This strongly supports the hypothesis that the relaxation of the acyl radical is associated with the rotation of C=O group.

The proposal that the spin-rotation relaxation of the acyl moiety is the main channel of ISC in acyl-containing biradicals also explains some previous observations that cannot be accounted for in the framework of a model based on ISR. For example, at room temperature the lifetimes of acyl−benzyl biradicals do not show significant dependence on the biradical length, even when it is varied from 7 to 15 C−C bonds between the radical centers.[10] A similar result has been obtained in the present work: at room temperature the lifetimes of 1,14-acyl−benzyl and 1,12-acyl−ketyl biradicals coincide, as well as the rate constants for polarization decays of a 1,14-acyl−benzyl and a 1,10-acyl−alkyl biradical at low temperatures. If SOC-induced IRS in the biradical were responsible for intersystem crossing in the high-temperature region, the contribution of closed conformations to the total inter-radical distance distribution for shorter biradicals would be much greater, and one would expect much faster decay of shorter biradicals (IRS is effective only in close conformations).

Spin-rotation relaxation associated with the rotation of the $-C{=}O$ group also explains the reported difference between TREPR spectra of saturated and unsaturated acyl radicals. The spectra of saturated acyl radicals are reported to be broad and have little resolved structure.[30,58] The same feature can be observed also for the SCRP spectra of acyl-containing biradicals (see Figure 4 and refs 6, 27, and 39: line broadening due to short relaxation times (for spin-rotation relaxation one can presume $T_1 = T_2$) smears out the hyperfine structure. At the same time, Davies et al. reported narrow well resolved spectra of acyl radicals in which the $C{=}O$ group is attached to an unsaturated moiety.[59,60] This can be accounted for as the conjugation between the $-C{=}O$ group and the neighboring π-system, which increases the energetic barrier for internal rotation and significantly increases the relaxation time.

Conclusions

Contrary to the well-established viewpoint that the main source of intersystem crossing in flexible acyl-containing biradicals is spin−orbit coupling, which mediates the triplet-state reactivity of biradicals, in this work strong evidence has been obtained that it is the relaxation of the acyl moiety of the biradical that determines the rate of ISC. The relaxation time does not depend on molecular size, solvent viscosity, and applied magnetic field, and its correlation time has a very small activation energy, $E_u = 8.9$ kJ/mol. This relaxation has been attributed to the spin-rotation mechanism associated with the internal rotation of the carbonyl group.

Combined application of TREPR and LFP methods allowed us to separate molecular and spin dynamics and to determine the activation energies of both processes. From good agreement of the experimental data with the results of model simulations we are convinced that time-resolved study of SCRP polarization kinetics is a reliable way to measure the relaxation times of fast-relaxing radicals such as acyl-containing biradicals.

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