Consecutive Biradicals during the Photolysis of 2,12-Dihydroxy-2,12-dimethylcyclododecanone: Low- and High-Field Chemically Induced Dynamic Nuclear Polarizations (CIDNP) Study

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Received: November 20, 1997; In Final Form: March 5, 1998

Low- and high-field ^{1}H chemically induced dynamic nuclear polarizations (CIDNP) have been applied to investigate geminate reactions of consecutive biradicals generated during the photolysis of 2,12-dihydroxy-2,12-dimethylcyclododecanone. The detailed mechanism of the reaction is established. It is shown that the fast chemical transformation (decarbonylation) of the primary acyl-ketyl biradical manifests itself in CIDNP effects in low and high magnetic fields: the difference in the CIDNP field dependencies for the products of the primary and secondary biradicals is observed, and the net and multiplet effects for the products of the secondary bis-ketyl biradical develop in different time scales. The first observation of the CIDNP "memory effect" in biradical reactions is reported. Model calculations of the CIDNP kinetics based on the numerical solution of the stochastic Liouville equation for the Fourier transform of the biradical spin density matrix have been performed, and a good agreement between the theoretical calculations and experimental data has been found.

Introduction

Radical pairs as reaction intermediates are usually created in a spin-correlated electronic-spin state (singlet or triplet) from a precursor molecule of the same multiplicity (singlet or triplet) via spin-conserving chemical reactions. Singlet−triplet transitions in the radical pair driven by electron−nuclear spin interactions, and the difference in recombination probability for singlet and triplet state give rise to the effects of chemically induced dynamic electron (CIDEP) and nuclear (CIDNP) polarizations in radical reactions that can be used as powerful tools for investigation of chemical reactions.

Flexible biradicals generated during the photolysis of cyclic ketones represent an excellent model of long-lived radical pairs with restricted mobility and have been widely used for the investigation of the interradical interactions in geminate processes by the methods of magnetic resonance and optical spectroscopy.[1−8] It has become clear that any experimental result, whether it is an electron paramagnetic resonance (EPR) spectrum,[2,3b] or kinetics of electron[4] or nuclear polarization,[5,6] or magnetic field dependencies of CIDNP[3,7] and biradical lifetime,[3,8] is determined by the whole totality of interactions in biradical: Zeeman, hyperfine, spin−orbit, exchange interactions, the mutual movement of radical centers, and so on. Thus, the quantitative evaluation of the parameters of these interactions from the results obtained with the single experimental technique becomes rather difficult. In this situation, the use of complementary methods looks more promising.

Nuclear polarization formed in flexible biradicals was studied earlier by stationary[3d,3e,4,7] and time-resolved[5,6] methods. It has been shown that the CIDNP in the reactions of biradicals with the chain length of 11−12 C−C bonds in magnetic fields of a few Tesla is formed purely due to S−T_0 transitions, whereas in low magnetic fields, the CIDNP effects correspond to an S−T_- mechanism. In an ongoing project we extended our study of biradicals to the case when, during its evolution, a primary biradical undergoes a chemical transformation. These reactions can serve as model systems for investigation of singlet−triplet evolution of consecutive radical pairs (RPs). Chemical transformation changes the magnetic interactions of the RPs, and singlet−triplet evolution of every RP depends on the whole history of the precursor RPs, even if some of them are too short-lived to be directly detected by modern time-resolved magnetic resonance techniques. If the rate of the chemical transformation is slow compared with the rate of intersystem crossing in the biradical, the products of the secondary biradical demonstrate the "escape" polarization, the sign of which is opposite to the sign of the primary biradical products.[9] Here, we studied the situation when the chemical transformation is fast, and revealed the CIDNP "memory effect", which was earlier observed in the reactions of consecutive RPs.[10−12]

In our recent work,[4] we applied three different methods, time-resolved EPR (TR EPR), CIDNP, and laser flash photolysis (LFP), for the investigation of acyl-ketyl and bis-ketyl biradicals generated in the photolysis of cyclododecanones with methyl and hydroxyl substituents in α-positions. The spin-correlated radical pair (SCRP) spectra, the kinetics of SCRP polarization, and the magnetic field dependencies of CIDNP and of biradical lifetimes have been obtained. All the results obtained were treated within the frames of the theoretical model introduced by de Kanter and co-workers.[13] A common set of the parameters has been found for the interactions in these biradicals that allows a common description of all experimental data. In the present work, we continue to study these biradicals by the time-resolved CIDNP method. The aims were to establish in detail the reaction pathway for the photolysis of 2,12-dihydroxy-2,12-dimethylcyclododecanone (**I**), to investigate the kinetics of CIDNP in the fast geminate consecutive reactions, and to

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S1089-5639(98)00271-0 CCC: $15.00

check whether the kinetics of nuclear polarization at high magnetic field is compatible with the same set of parameters.

Experimental Section

A detailed description of our TR CIDNP setup was given earlier.[6c,9] A sample, purged with argon and sealed in a standard NMR Pyrex tube, was irradiated by a COMPEX Lambda Physik excimer laser (wavelength 308 nm, pulse energy up to 150 mJ) in the probe of an MSL-300 Bruker NMR spectrometer. For the improvement of the time resolution, a homemade double-frequency resonator with the switching Q-factor was used instead of the commercial NMR probe. The TR CIDNP experiments were carried out using the usual pulse sequence: saturation − laser pulse − evolution time − detection pulse − free induction decay. The length of the detection pulses was 150 ns, which corresponds to the flip angle of ∼7°. The corresponding mathematical treatment of the experimental data, taking into account the length and the shape of rf-pulse,[14] allowed improvement of the time resolution up to 30 ns. Net and multiplet CIDNP effects were measured from the CIDNP spectra as the sum and the difference, respectively, of the integrated intensities of positive and negative spectral lines of each multiplet.

Low-field CIDNP measurements were performed using a setup described elsewhere.[15] The solutions were irradiated inside a homemade magnet by pulses of the COMPEX-110 excimer laser (308 nm) and then were transferred by a flow system into the probe of the MSL-300 NMR spectrometer. The transfer time was ∼2 s.

Synthesis of 2,12-dihydroxy-2,12-dimethylcyclododecanone was accomplished as described earlier.[16] Deuterated solvents methanol and acetonitrile (“Isotop”) were used as received.

Results and Discussion

CIDNP experiments were carried out using two deuterated solvents, methanol (CD_3OD) and acetonitrile (CD_3CN). The CIDNP spectra and CIDNP field dependencies obtained for both solvents turned out to be practically identical, except for a small “solvent shift” observed for some lines.

The (a) NMR spectrum of the starting ketone **I** in CD_3CN, the (b) TR CIDNP spectrum obtained 5 μs after the laser flash at the magnetic field $B_0 = 7$ T in CD_3OD, and the (c) CIDNP spectrum obtained during the photolysis of **I** at the magnetic field $B_0 = 10$ mT in CD_3CN are shown in Figure 1. In our TR CIDNP experiments, the Boltzmann polarization is suppressed due to the train of saturating pulses, so the spectrum b represents only polarized signals, whereas spectrum c gives the low-field CIDNP spectrum with a contribution from thermal polarization.

In our previous paper,[4] we showed that the photolysis of **I** proceeds via the Norrish type I cleavage of the starting ketone followed by the fast decarbonylation of the primary acyl-ketyl biradical ($k_{CO} \geq 5 \times 10^7$ s^{-1}) with the formation of the secondary bis-ketyl biradical. Both biradicals can recombine or disproportionate yielding the numerous diamagnetic products (Scheme 1). The assignment of the CIDNP signals is shown in Figure 1, where «′» denotes cis isomers. Some of the signals (for example, 2, 3, 7, and 8) have contributions from the products of both primary and secondary biradicals, making the quantitative determination of the product partition rather difficult. However, careful analysis of the CIDNP signs and kinetics for different lines (vide infra) allows one to determine the general scheme of the photolysis of **I** (Scheme 1). The main channels of the primary acyl-ketyl biradical decay (except decarbonylation) are the recombination with the restoration of the initial compound in both trans and cis forms (signals 9 and 9′), and the disproportionation yielding the linear molecules with the aldehyde (signal 1) and enol (signals 2, 3, 7 and 8) *termini* (products **II** and **III** in Scheme 1). For the secondary bis-ketyl biradical, the recombination yields cyclic compound **VII** (signals 10 and 10′), and products of disproportionation are the molecules with the alcohol (signals 4 and 11) and enol (2, 3, 7 and 8) or ketone (5 and 6) *termini* (products **IV**, **V**, and **VI**).

At the magnetic field of 10 mT, the main channel of CIDNP formation is the intersystem crossing due to S−T₋ mixing.

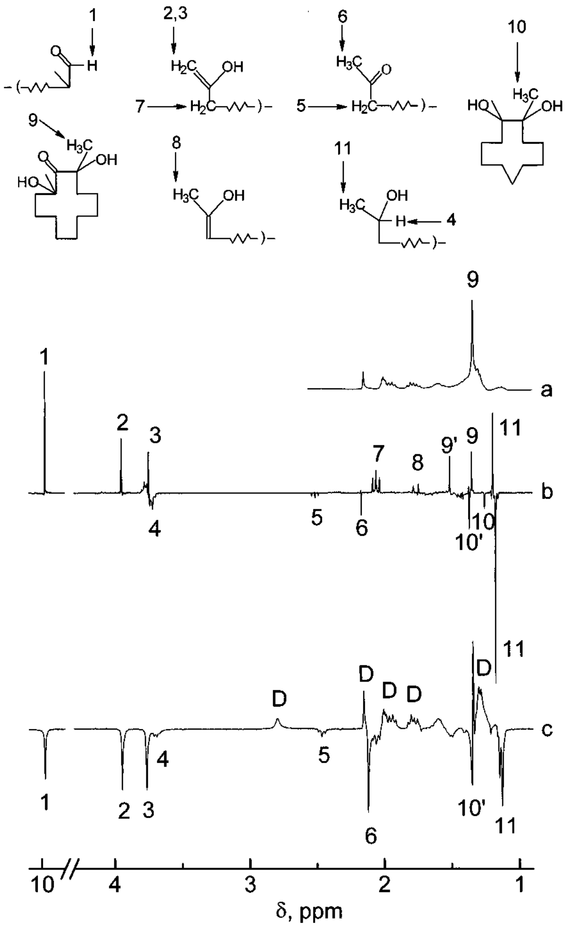
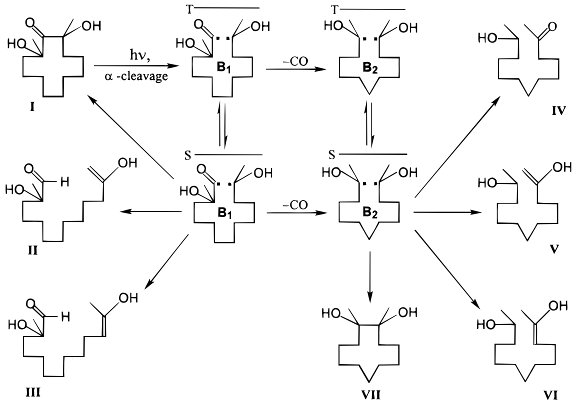


Figure 1. ^{1}H NMR spectra obtained during the photolysis of **I**: (a) NMR spectrum of **I** in CD_3CN before irradiation; (b) CIDNP spectrum during the photolysis of **I** at the magnetic field 7 T in CD_3OD at the delay time between laser and rf pulse of 5 μs; (c) NMR spectrum during the photolysis of **I** at the magnetic field 10 mT in CD_3CN. Numbers indicate the assignment of the lines, “D” corresponds to the equilibrium signals of the solvent and starting ketone.

SCHEME 1



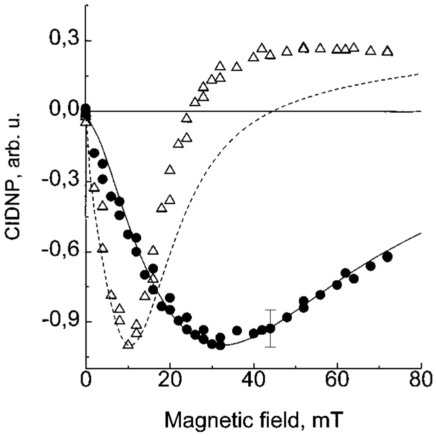


Figure 2. Normalized CIDNP field dependencies obtained during the photolysis of I: (△) for aldehyde proton of the products **II** and **III** (signal 1) of primary biradical; (●) for ketone protons of the product **IV** (signal 6) of secondary biradical. Solid and dashed lines − model calculations (see text).

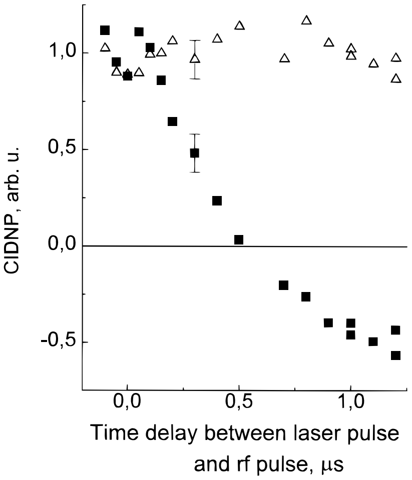


Figure 3. Experimental kinetics of the CIDNP net effect: (△) for the aldehyde proton of the products **II** and **III** (signal 1) of primary biradical; (■) for the **C**$\mathbf{H_3}$CH(OH) protons of the products **IV**, **V**, and **VI** (signal 11) of secondary biradical.

Correspondingly, all polarized signals have an emissive character. Figure 2 represents the CIDNP field dependencies observed for the aldehyde product (signal 1) of the primary acyl-ketyl biradical (△) and for the ketone product (signal 6) of the secondary bis-ketyl biradical (●). The calculation of the CIDNP field dependence for the products of bis-ketyl biradical, which is shown in Figure 2 (solid line), has been described in our previous work,[4] so we refer the reader to this publication. Here, we only want to stress the difference between field dependencies for the products of the primary and secondary biradicals.

Earlier,[4] it was revealed that the CIDNP field dependencies, observed during the photolysis of 2-hydroxy-2,12-dimethylcyclododecanone (ketone with only one hydroxy substituent), are practically identical for the products of both primary and secondary biradicals. This result can be understood by taking into account the low rate of the decarbonylation ($k_{CO} = 4.2 \times 10^5$ s^{-1})[9] of the primary acyl-ketyl 1,12-biradical in which the intense nuclear polarization is formed. After decarbonylation, this polarization is transferred to the secondary alkyl-ketyl 1,11-biradical. In this biradical, some CIDNP is formed; however, this additional polarization is small compared with the polarization formed in the primary biradical. Thus, the CIDNP field dependencies for the products formed in the two branches of the reaction pathway were very similar.[4]

In contrast to the results just presented, there is a remarkable difference in the CIDNP field dependencies for the products of the primary and secondary biradicals observed during the photolysis of **I** (Figure 2) in the present work. The relatively narrow curve with the emissive maximum at 10 mT, observed for the products **II** and **III** corresponds to the polarization created in 1,12-biradical.[4,6c,7d] Due to the fast decarbonylation, only a small fraction of primary biradicals have time to undergo the intersystem crossing; as a result, the polarization transferred to the secondary biradical is small, and the main part of the polarization of the products **IV**−**VII** is formed in the secondary 1,11-biradical. For this polarization, the broader field dependence and the shift of the polarization maximum to 30 mT are typical.[7]

It is also seen in Figure 2 that the polarization of the products of the primary biradical changes its sign from emission to enhanced absorption when the magnetic field increased to 25 mT. A reasonable explanation to this fact is the formation of nuclear polarization by $S-T_0$ mechanism. According to Kaptein's rules[17] for CIDNP, the sign of net polarization of the aldehyde proton formed by $S-T_0$ mechanism is positive: the aldehydes **II** and **III** are formed in the geminate reaction; the precursor of the biradical is triplet; $\Delta g > 0$ (g factors estimated from the corresponding monoradicals are 2.0032 for ketyl and 2.0008 for acyl *termini*);[18] hfi constant $A > 0$ ($A_{CH_2} = +1.94$ mT, $A_{CH_2} = +1.68$ mT).[18] The decarbonylation plays a role of a spin-sorting reaction: it "cuts off" the relatively slow transitions, decreasing the contribution of $S-T_-$ mechanism and significantly increasing the contribution of $S-T_0$ polarization. As a result, decarbonylation allows us to observe the CIDNP formed by $S-T_0$ mechanism at magnetic fields >25 mT, whereas at low field the contribution from $T_- - S$ is predominant.

We attempted to simulate the CIDNP field dependence for the products of the primary acyl-ketyl biradical using the same procedure and the same set of parameters as in our previous publication.[4] The decarbonylation was taken into account as the decay of the primary biradical disregarding its electron and nuclear spin state with the rate constant $k_{co} = 10^8$ s^{-1}, which corresponds to the decarbonylation rate constant for the $(CH_3)_2(OH)C\dot{C}O$ radical.[12] The result of the calculation is shown in Figure 2 (dashed line). The calculation procedure reproduces the observed CIDNP field dependence only qualitatively. According to our calculations, CIDNP formed by the $S-T_0$ mechanism grows with increasing magnetic field strength. However, the experimentally detected CIDNP reaches a constant value at the magnetic field of 50 mT. So far, we have not found an explanation for this discrepancy.

Figure 3 shows the kinetics of the net nuclear polarization at magnetic field 7 T for the products **II** and **III** (aldehyde proton; △) and **IV**−**VI** (methyl protons; ●). The absorptive CIDNP signal of aldehydes **II** and **III** stays unchanged up to 1 μs and longer. This result is consistent with the earlier results that the decarbonylation reaction of the primary biradical is faster than our time resolution (~30 ns). The positive CIDNP sign for aldehyde proton is in accordance with Kaptein's rules (vide supra). The net absorption of the secondary biradical products is the consequence of the fast decarbonylation of the primary biradical leading to the CIDNP "memory effect". This effect was predicted and first observed experimentally by R. Kaptein.[10a] The essence of the "memory effect" is that the spin coherency is transferred from the primary to the secondary radicals if the rate of the chemical transformation of the primary radical pair into the secondary one can compete with the rate of the geminate processes. As a result, the signs of nuclear polarization for the

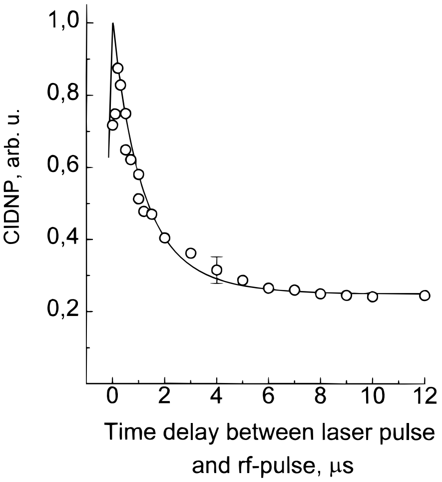


Figure 4. Kinetics of the CIDNP multiplet effect: (solid line) the calculated CIDNP kinetics for the product of disproportionation of bis-ketyl biradical; (○) experimental kinetics for the C**H$_3$**CH(OH) protons of **IV**, **V**, and **VI** (signal 11).

products of the primary and secondary radical pair coincide. In practice, the CIDNP "memory effect" was observed only in a few radical reactions.[10−12] Here, we report the first observation of the "memory effect" in the reactions of biradicals. The secondary bis-ketyl biradical is symmetrical, and no additional net polarization can be formed in this biradical. Thus, the protons of the secondary biradical carry the polarization of the opposite sign (emission) and, without "memory effect", the CIDNP sign of the products of this biradical should be negative. Namely, this situation has been observed in our previous works,[6c,9] where the decarbonylation rate of the primary biradical was slow compared with the rate of S−T$_0$ mixing: the polarization signs of the products of primary and secondary biradicals were opposite at any moment of observation. In the present case, however, immediately after the laser irradiation of **I**, the polarization of the products **IV**−**VI** is of absorptive character, and changes its sign to the emission only 0.5 μs after the laser pulse (Figure 3). The initial absorption for these products corresponds to CIDNP "memory effect", and the observed CIDNP kinetics reflects a very interesting situation: the subensembles of the secondary biradical with the positive projections of the nuclear spins have larger portions of the singlet character, whereas the total net polarization in the secondary biradical, and, correspondingly, in the product at the infinite time point, are emissive. The latter is explained on the basis of the decay of the subensembles with the positive projections of the nuclear spins in the primary biradical.

Figure 4 shows the kinetics of the multiplet CIDNP effect observed for the methyl protons of the products **IV**, **V**, and **VI** (signal 11). The multiplet effect of *A*/*E* type in these products is formed in the secondary symmetric bis-ketyl biradical due to the correlation of the nuclear spins belonging to the different ketyl moieties of the same biradical. Because S−T$_0$ transitions take place without nuclear spin flips, and the complete separation of the radical centers in the biradical is impossible; in the absence of the nuclear relaxation and side reactions, the nuclear polarization should reach its maximum determined by the rate of S−T$_0$ intersystem crossing and then decay to zero with the rate of the electron relaxation mixing the three triplet sublevels of the biradical. The nonzero value of the nuclear polarization at the infinite time points to the rather short nuclear relaxation time of about a few tens of microseconds. Another possible explanation for this effect is that the bimolecular encounters of biradicals could lead to the formation of ketyl monoradicals. This reaction was observed in our LFP experiments.[4] These monoradicals can carry the polarization of *E*/*A* type, resulting in nonzero stationary polarization of the 1,11-bis-ketyl biradical products; however, under our experimental conditions it is unlikely because we have not observed any dependence of the kinetic curve on the laser pulse intensity. Taking into account that nonzero stationary nuclear polarization has been observed earlier for the products of acyl-alkyl and acyl-ketyl biradicals,[6,9] and that the reported nuclear relaxation time of the ketyl monoradicals is hundreds of microseconds,[12] we can conclude that the short nuclear relaxation time T_1^{N} is the characteristic feature of biradicals.

The comparison of Figures 3 and 4 shows that the net and multiplet effects, recorded on the same protons of the same product of the secondary bis-ketyl biradical, develop in different time scales: the net polarization becomes constant ∼1 μs after the laser pulse, whereas the evolution of the multiplet polarization lasts five times longer than that of net polarization. The reason for this difference is that the net and the multiplet polarization have different origins. The net polarization is formed in S−T$_0$ mixing of the primary biradical, and then is transferred to the secondary one. Thus, only those bis-ketyl biradicals that immediately after the decarbonylation were in the T$_0$ state (or, more accurately, in the mixed S−T$_0$ states)[2] carry the net polarization. Recombination of these biradicals leads to the formation of the net CIDNP in the diamagnetic products. Thus, the time of the net polarization evolution corresponds to the rate of the decay of the biradical T$_0$ state. On the contrary, the multiplet polarization is formed in S−T$_0$ mixing of the secondary biradical. In high magnetic field, the rate of S−T$_0$ mixing is much faster than the rates of S−T$_+$ and S−T$_-$ transitions, so the populations of the T$_+$, T$_-$ states become significantly higher than that of T$_0$ state (in particular, it manifests itself as a strong SCRP polarization observed in these biradicals[4]). The electron relaxation, linking T$_0$ with T$_+$ and T$_-$ states of biradical, feeds the T$_0$ sublevel and prolongs the formation of the nuclear multiplet polarization. In other words, the kinetics of multiplet polarization reflects the decay of T$_+$ and T$_-$ sublevels of biradical, which is mainly determined by the rate of electron relaxation. Thus, the TR CIDNP method gives the unique opportunity to observe separately the evolution of the different states of the biradical: the kinetics of the net effect corresponds to the decay of T$_0$ sublevel, and the kinetics of the multiplet effect reflects the decay of T$_+$ and T$_-$ states!

It is noteworthy that the kinetics of nuclear polarization in the products of bis-ketyl biradical is prolonged in time compared with earlier reported CIDNP kinetics in the products of acyl-alkyl[6] and acyl-ketyl[9] biradicals. This fact is in agreement with the predominant role of spin−orbit coupling (SOC) in the intersystem crossing of biradicals with the acyl radical center. As a result, spin evolution of these biradicals at high magnetic fields takes hundreds of nanoseconds.[6,9] In bis-ketyl biradicals, SOC is of less importance,[4] and CIDNP kinetics for their products develops in the microsecond time scale.

In our previous work,[4] we studied the same bis-ketyl biradicals using complementary methods: TR EPR, low-field CIDNP, and LFP. The quantitative modeling was carried out by the solution of the stochastic Liouwille equation for the biradical spin density matrix taking into account the hyperfine interactions in biradical, distant-dependent exchange interaction, electron relaxation, SOC, the conformational movement of the polymethylene chain, and the reactions of the biradical from the singlet state at the closest interradical distance. It was shown that all the experimental data (namely, the SCRP spectrum and the kinetics of SCRP polarization, the CIDNP field dependence, and the dependence of biradical lifetime on the magnetic field) can be described with the common set of the parameters. Here, we tried to describe the kinetics of the multiplet polarization within the frames of the same model with the same set of the parameters. Calculation of the net CIDNP kinetics for the products of bis-ketyl biradical using the formalism of the spin density matrix is rather complicated by definition of the initial conditions for the secondary biradical. Simulation of this curve would be very time consuming: one should solve the equations for the primary biradical and then use this solution as the initial conditions for the secondary one. More important, the net effect in this system is not very large, and the obtained data (Figure 3) have a poor signal/noise ratio. In this situation, we restrict ourselves with the qualitative explanations only. Thus, only the experimental points are presented in Figure 3.

In calculation of the kinetics of multiplet CIDNP, the only difference between the models used in our previous paper[4] and this work is that to reproduce the nonzero value of the polarization at the infinite time we have introduced the transition between nuclear subensembles due to the fast nuclear relaxation in biradicals (vide supra). For simplification, all five magnetic nuclei at each end of the biradical were considered equivalent with the hfi constant $A = +1.8$ mT. The parameters taken from our previous work were: the recombination rate constant from the singlet state at the smallest interradical distance, $k_r = 10^{11}$ s^{-1}; the recombination rate constant from triplet states at the smallest interradical distance, induced by SOC, $k_{soc} = 8 \times 10^7$ s^{-1}; the parameters of exchange interaction, $J_0 = -1.3 \times 10^9$ mT, and $\alpha = 2.14$ Å^{-1} ($J = J_0 e^{-\alpha r}$); the effective diffusion coefficient $D = 2 \times 10^{-5}$ cm^2/s; the parameters of uncorrelated electron relaxation $G = 8 \times 10^{16}$ s^{-2} and $\tau_u = 10^{-12}$ s (here G characterizes the fluctuations of the local magnetic fields, $G = {}^1/_2\gamma^2 h^2 \langle |B_i|^2 \rangle$, induced by modulating the anisotropy of hyperfine interaction, and τ_u is rotational correlation time of radical centers); the correlation time for the rotation of the whole biradical, $\tau_c = 8 \times 10^{-11}$ s, which determines the rate of correlated electron relaxation (i.e., the relaxation induced by the dipole–dipole interaction of the radical centers) between triplet states in biradical; and $m = 200$, the number of slices of biradical end-to-end distribution function.

The only fitting parameter was the nuclear relaxation time T_1^N. The best fit shown in Figure 4 (solid line) was obtained with $T_1^N = 22$ μs. A good agreement between experimental data and calculations (Figure 4) shows that our theoretical model and the set of the parameters used here and in our previous paper[4] describe the kinetic behavior of biradicals fairly well.

Summary

Fast chemical transformation of biradicals (decarbonylation) has been shown to affect the formation of CIDNP in the products of both primary and secondary biradicals during the photolysis of 2,12-dihydroxy-2,12-dimethylcyclododecanone. CIDNP field dependencies for the products of the primary and secondary biradicals are different, and the shape of these curves depends on the rate of decarbonylation. At high magnetic field, the CIDNP "memory effect" is observed for the products of the secondary biradical, which is formed due to conservation of spin coherency in the decarbonylation of the primary biradical. It has been shown that for the products of the secondary biradical, the kinetics of net nuclear polarization correspond to the decay of the T$_0$ sublevel, and the kinetics of the multiplet CIDNP reflects the decay of the T$_+$ and T$_-$ states. Thus, the CIDNP method can be successfully applied to the study of chemical reactions that are much faster than the time resolution of the method.

The important result of this work is that the good agreement between experimental CIDNP kinetics and the numerical simulation was obtained with the same set of parameters as we used earlier[4] for the simulation of the CIDEP spectrum and kinetics and field dependencies of CIDNP and biradical lifetime. This result confirms that our theoretical model and the chosen set of parameters describe well the spectroscopic and kinetics features of biradicals.

Acknowledgment. This work was supported by Russian Foundation for Basic Research (Project No. 96-03-32930) and by INTAS (Project No. 96-1269). The authors thank Prof. Malcolm D. E. Forbes (University of North Carolina, Chapell Hill, NC) for the generous gift of 2,12-dihydroxy-2,12-dimethylcyclododecanone, and A.V.Y. thanks Prof. H.-M. Vieth (Free University of Berlin, Germany) for helpful discussion at the final stage of this paper preparation.

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