^{1}H and ^{13}C Nuclear Polarization in Consecutive Biradicals during the Photolysis of 2,2,12,12-Tetramethylcyclododecanone

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CIDNP effects arising in the geminate evolution of consecutive biradicals formed during the photolysis of 2,2,12,12-tetramethylcyclododecanone were investigated by the low- and high-field ^{1}H and ^{13}C CIDNP and time-resolved ^{1}H CIDNP methods. The ^{1}H field dependence of nuclear polarization induced in the recombination and disproportionation products of the consecutive biradicals as well as the ^{13}C CIDNP spectra at low and high magnetic fields was analyzed. It was confirmed that two types of biradicals (acyl−alkyl and bisalkyl) of different chain lengths contribute to the spin polarization. Model calculations of the geminate recombination kinetics were 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 allowed us to reveal all chemical transformations of the alkyl−acyl and bisalkyl biradicals and to estimate the probability of the "hidden" recombination of the biradicals to the starting ketone, as well as to determine the product distribution.

1. Introduction

CIDNP effects observed in radical reactions in solutions, where one of the members of a radical pair (RP) undergoes a chemical transformation ($[\dot{R}_1\dot{R}_2] \rightarrow [\dot{R}_1\dot{R}_3]$), were investigated by many authors.[1−5] If the chemical transformation is sufficiently fast and can compete with geminate processes, a so-called CIDNP "memory effect" is observed. In this case, the signs of polarizations arising in the primary ($[\dot{R}_1\dot{R}_2]$) and secondary ($[\dot{R}_1\dot{R}_3]$) radical pairs coincide.[1−4] Recently, this effect has been observed in the photolysis of 2,4-dimethyl-2,4-diphenylpentan-3-one and 1,1,3,3-tetraphenylpronan-2-one[6] and 2,4-dihydroxy-2,4-dimethylpentan-3-one.[7]

In contrast, in the case of the low rate of chemical transformation, which is considered in this work, the secondary radical pair is formed in the nuclear spin states that have not reacted in the primary pair. Thus, the products of the secondary pair carry the escape-type polarization, which is opposite in sign to the geminate one.[5] This is typical for the S−T$_0$ mechanism of CIDNP generation.

Of particular interest is the case where chemical transformations occur in a radical pair whose radical centers are linked by a polymethylene chain,

$$\dot{R}_1(CH_2)_n\dot{R}_2 \rightarrow \dot{R}_1(CH_2)_n\dot{R}_3$$

Since, in this case, the diffusion separation of the radical centers is inhibited, the S−T$_0$ approximation implies that the time evolution of CIDNP passes through a maximum and after a long time vanishes, making the stationary CIDNP inobservable. Addition of a scavenger, which sorts the products into geminate ones and the products of scavenging, gives rise to a non-zero stationary nuclear polarization.[8,9] The chemical transformation mentioned above can act as a scavenging reaction, but it does not stop the biradical spin evolution.

In this paper, we report on a CIDNP study of the reactions of biradicals resulting from the photoinduced α-C−C bond cleavage in 2,2,12,12-tetramethylcyclododecanone. The CIDNP effects in this compound in the presence of radical scavengers were studied by Turro and co-workers.[10] It has been confirmed that in ketones with methyl substituents in the α-position, the cleavage of the α-C−C bond (Norrish type I) dominates over the abstraction of γ-hydrogen by the acyl group (Norrish type II). It has also been shown that the primary acyl−alkyl biradical is subject to a small degree of decarbonylation,

$$(CH_3)_2\dot{C}(CH_2)_n\dot{C}(CH_3)_2CO \rightarrow (CH_3)_2\dot{C}(CH_2)_n\dot{C}(CH_3)_2 + CO$$

In the absense of radical scavengers, neither ^{1}H nor ^{13}C CIDNP was observed.[10] This fact was accounted for by the low rate of the decarbonylation reaction, which therefore can not serve as a spin-sorting process yielding stationary nuclear polarizations of different signs. It was believed that only addition of radical scavengers was able to induce a nuclear polarization in the reaction products of the primary biradicals. However, it was shown that the decarbonylation reaction serves as an isotopomer-sorting process, which slightly enriches one of the reaction products with ^{13}C isotope.[10] It has been established that both CIDNP and magnetic isotope effects originate from the dependence of the intersystem crossing rate on the nuclear spin configuration[11] and thus should occur simultaneously. Hence, the absence of the stationary CIDNP appears to be inconsistent with the magnetic isotope effects observed.

Turro et al.[10] chromatographically analyzed the photolysis products, which made it impossible to reveal the probability of the recombination of the biradicals to the starting ketone.

The acyl−alkyl and bisalkyl biradicals arising during the photolyses of α,α,α′,α′-tetramethyl-substituted cycloalkanones were extensively studied by TR ESR.[12−18] Strong effects of electron polarization were observed for both biradicals. Typically, the photolytic reaction was carried out under the conditions

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of predominant formation of one type of biradical, which was achieved by temperature variation.

All of the above suggests that some features of the photolytic reaction of 2,2,12,12-tetramethylcyclododecanone are still open to question. It seems to be interesting to ascertain whether the consecutive biradicals are formed during the photolysis of the starting ketone at room temperature, to determine the distribution of the products, and to estimate the probability of biradical recombination.

The above information can be readily obtained by the CIDNP method. Nuclear polarization arising in the primary biradical B_1 ($\dot{R}_1(CH_2)_n\dot{R}_2$) affects the induction of the nuclear polarization in biradical B_2 ($\dot{R}_1(CH_2)_n\dot{R}_3$). In the products of biradical reactions, the manifestation of the effect of B_1 on B_2 varies with the magnetic field. The use of low- and high-field ^1H and ^{13}C CIDNP in combination with the time-resolved CIDNP method can yield valuable data on the kinetics and mechanism of the reaction under study as well as on the magnetoresonance parameters of intermediate biradicals.

2. Experimental Section

The time-resolved CIDNP method is described elsewhere.[19] The time-resolved CIDNP setup has been described in detail earlier.[20] A sample in a commercial Pyrex tube was irradiated inside the probehead of an MSL-300 Bruker NMR spectrometer by an excimer laser (308 nm, pulse energy up to 120 mJ). The probehead was specially designed for the TR CIDNP experiments. Instead of the usual saddle-shape coil, a homemade double-frequency resonator was employed (observation frequency 300 MHz, lock frequency 46 MHz). During a transmitter cycle, at 300 MHz, the Q factor of the resonator was damped to 20−30 using a PIN diode; then, during the acquisition, the Q factor was restored to a value of 250−300. In the resonator, the amplitude of the rf field was increased by a homemade 300-MHz amplifier with a 1000-W output. Under these conditions, the $\pi/2$ rf pulse duration was 1.9 μs. Details of the resonator design will be published later. Kinetic measurements were carried out using the detection pulses with the fwhm of 150 ns, which corresponded to the 7° flip angle of the magnetization vector.

The stationary ^{13}C CIDNP spectra were obtained on a JEOL-90 FT NMR spectrometer under the irradiation of a high-pressure mercury lamp.

The ^1H CIDNP field dependence was studied by the field-cycling technique:[9] the sample was transferred between two magnets inside a double-tuned movable NMR probe. The mechanical system for the probe transfer is described elsewhere.[21] We used a pulsed flow system to change the sample after each irradiation cycle followed by the CIDNP detection. The low-field ^{13}C CIDNP spectrum was obtained by the same technique.

Tetramethylcyclododecanone was kindly supplied by Prof. M. D. E. Forbes (University of North Carolina). Solvents $CDCl_3$, $CHCl_3$, and hexane were purchased from Aldrich; cyclohexane-d_{12} was obtained from "Isotope".

The optical densities of solutions were kept below 0.5. Prior to irradiation, the samples were bubbled with argon gas for 5 min. The ketone concentration was $\approx 3 \times 10^{-2}$ M.

3. Theory

CIDNP Kinetics in the Geminate Recombination of Biradicals at Strong Magnetic Fields. CIDNP kinetics in geminate recombination of biradicals was described by various models.[22−25] Recently we proposed an approach to the description of the CIDNP kinetics in the geminate recombination of biradicals,[20] which involves the numerical solution of the stochastic Liouville equation taking into account the conformational statistics of the polymethylene chain. Our approach is based on the model developed by de Kanter et al.[26] for calculating the field dependence of CIDNP, which allows one to consider of the effects of medium parameters (viscosity, temperature, diffusion coefficient) on the CIDNP kinetics in an explicit form. According to this model, the normalized distribution of biradical end-to-end distances for all possible conformations of the polymethylene chain is divided into segments of equal areas. The relative motion of the radical centers is considered to be diffusional jumps between neighboring segments.[26] The relation between the spin and molecular dynamics through the exchange interaction, which depends on the distance between the radical centers, is taken into account.

It has been established in our previous paper[9] that in the geminate recombination of biradicals, the calculated CIDNP kinetics depends strongly on the number of segments of the function of biradical distribution over end-to-end distances. A small number of the segments ($\approx$20) give the overestimated size of the reaction zone (in calculations, it is a segment with the minimum separation of radical centers). As a result, the calculated lifetime of the biradicals is increased. The increasing number of segments (m) increases the calculated lifetime of the biradicals; however, beginning with $m \geq 200$, the lifetime is practically independent of m. Therefore, in calculations, we used the value $m = 400$.

The theoretical approach to the calculation of the above CIDNP kinetics was described in detail in our previous paper.[20] Therefore, below we outline it briefly.

The time evolution of the spin density matrix of a biradical is described by the stochastic Liouville equation

$$\frac{\partial \rho(t)}{\partial t} = -i\hat{L}\rho(t) + \hat{R}\rho(t) + \hat{W}\rho(t) + \hat{K}\rho(t) \qquad (1)$$

Here, $\hat{L}$ is the Liouville operator, $\hat{R}$ is the relaxation matrix, $\hat{W}$ characterizes the dynamic behavior of the polymethylene chain, and $\hat{K}$ represents the chemical reactions of the biradical. Matrices $\hat{L}$, $\hat{R}$, $\hat{W}$, and $\hat{K}$ were described in detail earlier.[26] The corrected $\hat{R}$ matrix was used.[27]

To calculate the CIDNP kinetics, we solved the stochastic Liouville equation for the Fourier transform $\tilde{\rho}(\omega)$ of the spin density matrix.[19] For $\tilde{\rho}(\omega)$, the time differentiation is reduced to multiplying by $i\omega$. The Fourier reconstruction of $\tilde{\rho}(\omega)$ yields a time-dependent density matrix, which allows the calculation of the CIDNP kinetics.

Substitution of the Fourier transform $\tilde{\rho}(\omega)$ into $\int_0^\infty \rho(t) e^{-i\omega t}\, dt$ into eq 1 gives the stationary equation for $\tilde{\rho}(\omega)$:

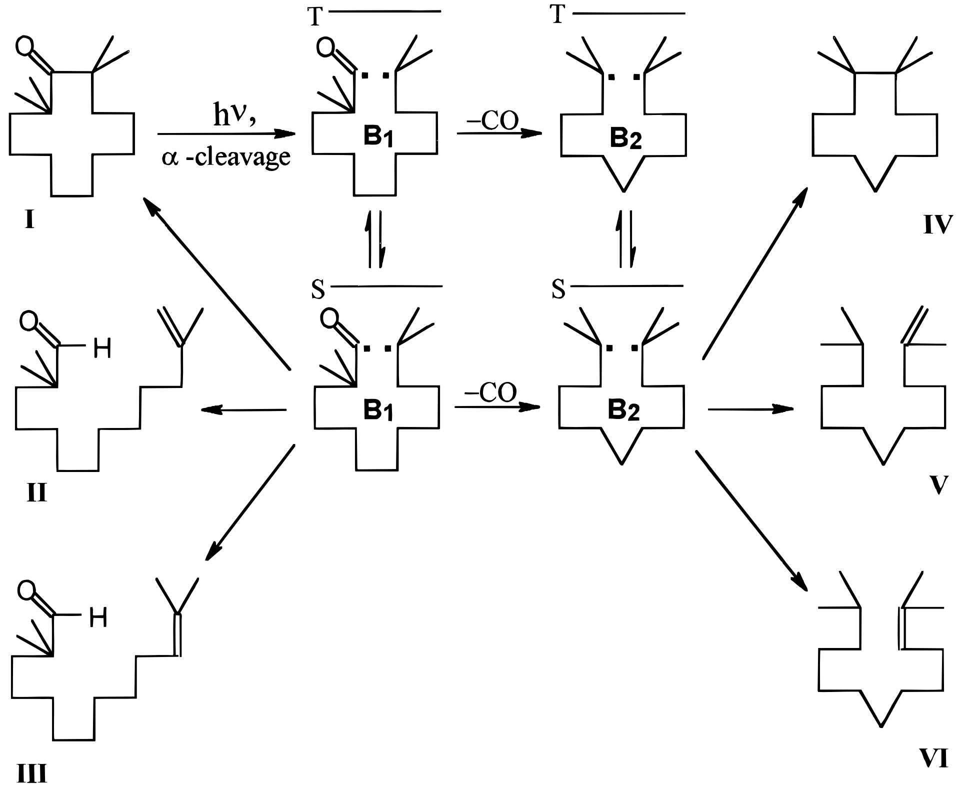
$$-\rho(t = 0) = i\omega\tilde{\rho}(\omega) - i\hat{L}\tilde{\rho}(\omega) + \hat{R}\tilde{\rho}(\omega) + \hat{W}\tilde{\rho}(\omega) + \hat{K}\tilde{\rho}(\omega) \qquad (2)$$

The following six elements of the spin density matrix are non-zero: ρ_{SS}, ρ_{ST_0}, ρ_{T_0S}, $\rho_{T_+T_+}$, $\rho_{T_0T_0}$, and $\rho_{T_-T_-}$. Solving eq 2 for different ω's, we obtain the Fourier spectrum $\tilde{\rho}(\omega)$. The next step is the numerical reconstruction of $\rho_{SS}(t)$ at the minimum separation of radical centers, $r = r_d$,

$$\rho_{SS}(t) = \omega_0/\pi\left[A(0)/2 + \sum_{k=1}^{\infty} A(k\omega_0)\cos(k\omega_0 t) - \sum_{k=1}^{\infty} B(k\omega_0)\sin(k\omega_0 t)\right] \qquad (3)$$

where $\omega_0 = 2\pi/T$; T is the time of spin evolution in the biradical, which is sufficient for the CIDNP of the final product to reach

SCHEME 1



a stationary value (the nuclear relaxation in the diamagnetic product is disregarded). On the basis of the experimental data, we took T as 2000 ns. In eq 3 the number of members in the series was 1000.

The values of $A(k\omega_0)$ and $B(k\omega_0)$ are related to the Fourier transform of the spin density matrix as follows:

$$A(k\omega_0) = \int_0^\infty \rho_{SS}(t)\cos(k\omega_0 t)\,dt = \mathrm{Re}[\tilde{\rho}_{SS}(k\omega_0)] \quad (4)$$

$$B(k\omega_0) = -\int_0^\infty \rho_{SS}(t)\sin(k\omega_0 t)\,dt = \mathrm{Im}[\tilde{\rho}_{SS}(k\omega_0)] \quad (5)$$

To calculate the polarization kinetics of a nucleus i, we averaged the values of $\rho_{SS}(t)$ obtained at $r = r_d$ for $I_{iz} = {}^1/_2$ and $I_{iz} = -{}^1/_2$ over all configurations of the other nuclear spins. It is assumed that the recombination from the triplet state is induced by the spin−orbit coupling, which directly transfers the triplet states of the biradical to the singlet state of the product at $r = r_d$. In the recombination products, for the ith spin, the rate of polarization change is

$$\frac{dP_i}{dt} = k_r[\bar{\rho}_{SS}|_{r=r_d,I_z=1/2} - \bar{\rho}_{SS}|_{r=r_d,I_z=-1/2}] + k_{soc}\sum_i[\bar{\rho}_{T_iT_i}|_{r=r_d,I_z=1/2} - \bar{\rho}_{T_iT_i}|_{r=r_d,I_z=-1/2}] \quad (6)$$

Here k_r and k_{soc} are the rate constants of biradical recombination from the singlet and triplet states, respectively, at $r = r_d$; T_i are the triplet sublevels of the biradical (T_0, T_+, T_-); horizontal lines mean averaging over the configurations of all nuclei except for the ith one. Integrating eq 6 allows one to obtain the CIDNP kinetics on the assumption of the instantaneous formation of the biradicals. This assumption is valid, since for α-methyl-substituted cycloalkanones, the triplet lifetime is rather short.[28−30]

In this work, we calculated the CIDNP kinetics of the acyl−alkyl biradicals arising in the photolysis of 2,2,12,12-tetramethylcyclododecanone. Eight equivalent protons were taken into account, since in the biradical the hfi constants of the protons of both CH_3 groups and the β-CH_2 group of the alkyl end practically coincide. Thus, the number of different nuclear configurations is nine. Model calculations were used to confirm the conclusions derived from the experimental data described in section 4.3.

4. Results and Discussion

It is well-known that in aliphatic ketones, the cleavage of α-C−C occurs from the excited triplet state. α-Substituents accelerate the α-C−C bond cleavage and induce decarbonylation. Thus, the photolysis of 2,2,12,12-tetramethylcyclododecanone can yield acyl−alkyl and bisalkyl biradicals, which can either recombine or disproportionate. This suggests that the photolysis of the ketone under study can proceed by Scheme 1.

Turro et al.[10] proposed the reaction scheme based on the analysis of the reaction products at relatively high degrees of decomposition of the starting ketone. The reaction products (aldehydes) were accumulated in amounts large enough to partly absorb the exciting radiation, and the main photochemical process was accompanied by side reactions. By contrast, our experimental conditions allowed us to avoid secondary reactions.

4.1. ^{13}C CIDNP at High and Low Magnetic Fields.

^{13}C CIDNP investigations at natural abundance of ^{13}C isotope yield information on the chemical transformations of molecules in photoreactions. For the alkyl−acyl biradical, the hfi constants of the carbon nuclei can be estimated from the corresponding values for the monoradicals: $A_{C=O} = 114$ G,[30] $A_{2-C} = 47$ G,[30] and $A_{12-C} = 46$ G;[31] for the biradical ends, the g factors are 2.0026 (alkyl moiety)[31] and 2.0008 (acyl moiety).[30] The presence of ^{13}C with a high hfi constant at any of three possible positions has no effect on the molecular dynamics and exchange interaction of the biradical electrons, but it significantly affects

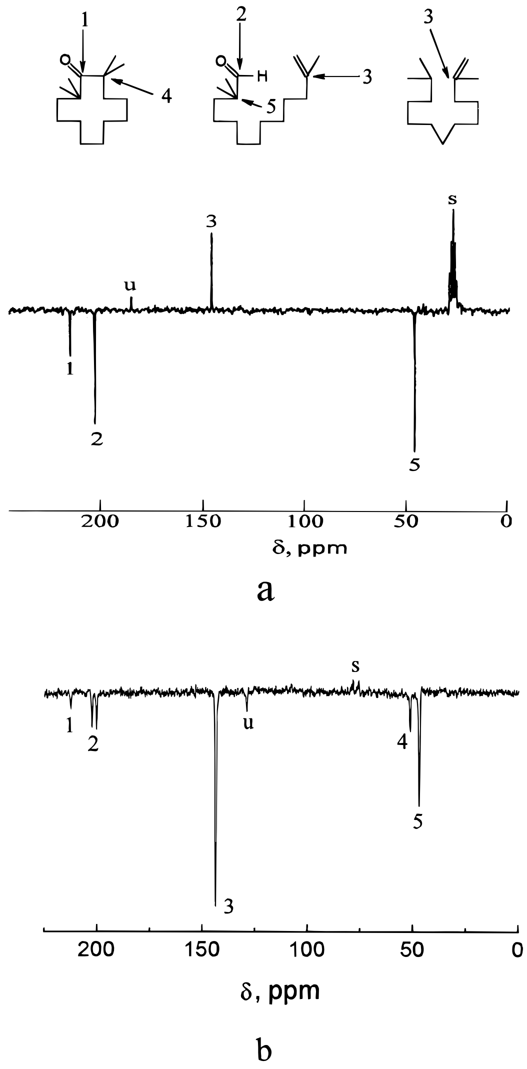


Figure 1. ^{13}C CIDNP spectra obtained during the photolysis of 2,2,12,12-tetramethylcyclododecanone (a) at the magnetic field 2.1 T in cyclohexane-d_{12}, ^{1}H decoupled, and (b) at the magnetic field 25 mT in chloroform; s, solvent, u, unrecognized signals.

TABLE 1: ^{13}C Chemical Shifts and CIDNP Signs at High Magnetic Fields for the Products of the Photolysis of 2,2,12,12-Tetramethylcyclododecanone in Cyclohexane-d_{12} (A, Enhanced Absorption; E, Emission)

no.	nucleus	compd and its no. in Scheme 1	chem shift, ppm	CIDNP sign
1	CO	I[a]	214.7	E
2	C(=O)H	II[b]	202.6	E
3	=CH$_2$	II[c]	145.7	A
		V[c]	145.7	
4	2-C	I	50.5	
5	2-C	II	45.7	E

[a] 2,2,12,12-Tetramethylcyclododecanone. [b] 2,2,12-Trimethyltridec-12-en-1-al. [c] 2,12-Dimethyltridec-1-ene.

the spin dynamics of the singlet−triplet transitions and can accelerate the electron relaxation.

The times of the nuclear relaxation of the carbon atoms vary significantly (by an order of magnitude and more) with substituents, since the main relaxation mechanism is the dipole−dipole interaction with neighboring protons. The quaternary and carbonyl carbon atoms have the longest times of nuclear relaxation T$_1$, and hence, in the ^{13}C CIDNP spectra obtained in the experiments with sample transfer and in the stationary experiments, the signals of these atoms are expected to be the most intense.

The CIDNP spectra obtained in our experiments are independent of the solvent. The ^{13}C CIDNP spectrum obtained at the magnetic field 2.1 T in C$_6$D$_{12}$ is shown in Figure 1a. The line assignment and CIDNP signs are given in Table 1. In contrast to the earlier results,[10] the intensities of the CIDNP signals are rather high even in the absence of radical scavengers. The signals observed correspond to the 1-C, 2-C, and 12-C of aldehyde II and to the carbonyl carbon atom of starting ketone I. In accordance with Kaptein's rules,[11] the signs of the polarizations correspond to the positive hfi constants of 1-C, 2-C, and 12-C of the intermediate biradical. Surprisingly, the polarized signal of the α-C atoms of the starting ketone is absent in the spectrum. However, using the values of the hfc for 2-C and 12-C of biradical B$_1$, we can explain this fact as follows. For 2-C and 12-C of the alkyl−acyl biradical, the values of Δg are opposite in sign, while the hfi constants practically coincide. Hence, at high fields, the polarizations of 2-C and 12-C are equal in magnitude and opposite in sign. The recombination of biradical B$_1$ to I makes 2-C and 12-C equivalent, with their polarizations mutually compensated. Thus, for starting ketone I, the signals of the α-C atoms are not observed, and the ^{13}C CIDNP spectrum exhibits only the emission signals of the carbonyl carbon atom of I.

In aldehyde II, the chemical shifts of 2-C and 12-C do not coincide, and their polarizations are observed separately. The CIDNP spectrum of aldehyde II involves the emission signal of 1-C, the enhanced absorption signal of 12-C, and the emission signal of 2-C.

Another interesting feature of the spectrum is the absense of signals from the products of bisalkyl biradical B$_2$. This could be explained by the same arguments as those used in the case of α-C atoms of the starting ketone. On decarbonylation, the oppositely polarized 2-C and 12-C atoms of the alkyl−acyl biradical B$_1$ transfer to the equivalent terminal 1-C and 11-C atoms of the bisalkyl biradical B$_2$, where $\Delta g = 0$, and there is no additional net polarization. The disproportionation reaction does not break the equivalence of the terminal C atoms, since the abstraction of a hydrogen atom group is equally probable from either of the methyls. Therefore, on the disproportionation or recombination of the bisalkyl biradical, the polarizations of 1-C and 11-C are compensated (products IV, V, and VI), and no consecutive biradicals are revealed.

At low magnetic fields, the nuclear polarization is considerably higher. Figure 1b shows the ^{13}C CIDNP spectrum obtained at the magnetic field 25 mT. The emission sign of the signals corresponds to the S−T$_-$ mechanism of CIDNP generation, which involves simultaneous flips of electron and one of nuclear spins from α to β spin states (T_α states transfer to Sβ irrespective of the sign of the hfi constant).[11] Different mechanisms of CIDNP generation at low and high magnetic fields are reflected in the CIDNP spectra. First, at low fields, the 2-C and 12-C atoms of the alkyl−acyl biradicals exhibit emission and make a net contribution to the signals of the α-C atoms of the starting ketone. Second, at 145.7 ppm, the relative intensity of the signal of alkene carbon increases. This cannot be explained by different relaxation times, since T$_1$ for the alkene carbon does not exceed that for the carbonyl carbon atom. The increased intensity of the signal of the alkene carbon is associated with the fact that at low fields, the 12-C atom of aldehyde II and the 2-C atom of compound V give emissive signals, and the resulting signal is a sum of these two signals. The assumed formation of the bisalkyl biradicals requires other supporting evidence.

4.2. Field Dependence of ^{1}H CIDNP. The field dependence of CIDNP is governed by the magnetoresonance parameters

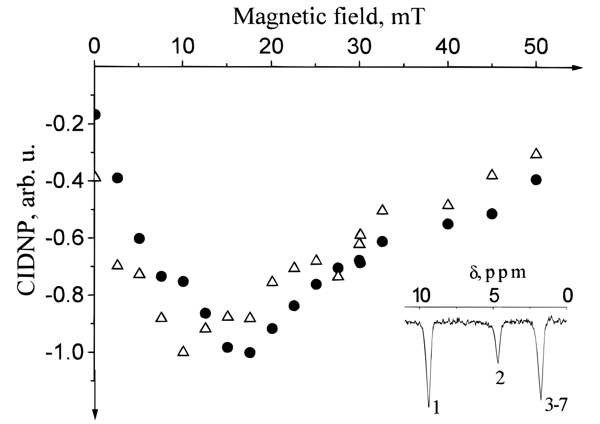


Figure 2. Plots for ^{1}H CIDNP as a function of the magnetic field: △, for signal 1 (aldehyde proton of II); ●, for signal 2 ($H_2C=$ protons of II and V); both curves are normalized to unity at the maxima. Insert: ^{1}H CIDNP spectrum obtained during the photolysis of 2,2,12,12-tetramethylcyclododecanone in $CDCl_3$ at the magnetic field 15 mT.

(exchange and hyperfine interactions) of intermediate biradicals, which makes it possible to follow the evolution of the consecutive biradicals. However, the stationary CIDNP spectra provide only qualitative information on the distribution of the products, since the absolute and relative line intensities depend strongly on the experimental conditions and relations between the irradiation time, sample transfer time, and the relaxation times of different nuclei.

At low magnetic fields, the ^{1}H CIDNP spectra exhibit three emission signals: a signal of the aldehyde proton, a signal of the alkene protons, and a broad emission signal within 1−2 ppm (Figure 2, insert). In the aliphatic region of the spectrum (1−2 ppm), we failed to separate reliably the contributions of different nuclei to the polarization because of the low spectral resolution of our setup for CIDNP studies at low magnetic fields.

Figure 2 shows the CIDNP as a function of the magnetic field for aldehyde and alkene protons. It is seen that the maxima of these two functions do not coincide. To explain this, we consider the mechanism of generation of CIDNP in the consecutive biradicals at low magnetic fields.

It is known that at low magnetic fields, the nuclear polarization results from the difference in the rates of the T_+-S and T_--S transitions.[11] For negative exchange interaction J, the T_--S transition predominates. The maximum effects of the spin polarization are observed at the magnetic fields with the T_--S mixing. In the T_--S intersystem crossing, one of the nuclear spins flips from the α projection to the β one. Thus, both recombination products and unrecombined triplet biradicals are enriched with the β projections of nuclear spins.

It is reasonable to assume that decarbonylation does not change the electron and nuclear spin states of the biradical. Thus, in the secondary biradical B_2, the triplet sublevels have nonequilibrium populations. In the secondary biradical B_2, the most efficient T_--S transition is suppressed due to the depletion of biradicals in the $T_-\alpha$ state. The bisalkyl biradical B_2 can get the singlet character and then recombine through the T_+-S and T_0-S transitions. However, the T_0-S transitions do not contribute to the CIDNP, and the T_+-S transitions are slow compared to the relaxation rate. The relaxation processes enrich the $T_-\alpha$ state, opening the possibility for the biradical to undergo the $T_-\alpha-S\beta$ transition and recombine. Thus, the net polarization induced in the products of the secondary biradical B_2 is emissive. However, since the biradical chain length is reduced by decarbonylation, the effective exchange interaction increases, and the CIDNP field dependence exhibits a maximum at a relatively higher magnetic field.

Since the chemical shifts of the $H_2C=$ protons of products II and V coincide, at low magnetic fields, it is impossible to isolate the contributions of different biradicals to the polarization of this signal. Therefore, the field dependence of the CIDNP signal of the alkene protons is a superposition of the CIDNP as a function of the magnetic field for two different biradicals. Its maximum is located between the corresponding maxima for the C_{11} and C_{12} biradicals (10 and 25 mT, respectively). Qualitatively, this is consistent with the above-mentioned manifestation of CIDNP in the consecutive biradicals. In the photolysis of 2,2,8,8-tetramethylcyclooctanone, the field dependence of CIDNP exhibited different for different products.[13]

It would be interesting to compare the field dependence shown in Figure 2 with the field dependence for the methyl protons of product V, which arises only in the recombination of the secondary biradical. For this purpose, we are working at increasing the spectral resolution of our apparatus.

4.3. ^{1}H CIDNP Kinetics at High Magnetic Fields. Decarbonylation can serve to sort the reaction products into the geminate and escape ones. In the intermediate biradical, eight quasiequivalent β-protons of the alkyl end ($(CH_3)_2$ and β-CH_2) have the hfi constant +23 G.[32] According to Kaptein's rules,[11] at high magnetic fields, the CIDNP spectrum of the geminate products should exhibit the enhanced absorption. Since the geminate and escape products should carry polarizations of different signs, the emissive signals could be direct evidence for the formation of the bisalkiyl biradicals.

The ^{1}H CIDNP spectrum obtained at coinciding laser pulse and the front edge of the rf pulse (4-μs duration) is shown in Figure 3. The signal assignment is given in Table 2. Products III and VI are not observed in our CIDNP spectra. This is consistent with the results of Weiss and Kochanek,[33,34] who observed a 10-fold predominance of the products with the “external” double bond.

The spectrum shows absorption signals 1−5 and emission signals 6 and 7. The presence of the signals from the methyl protons of the starting ketone points directly to the effective recombination of biradicals resulting in the formation of the starting ketone. The proton polarization of I and II is formed in the same biradical. In II, the polarization of six equivalent CH_3 protons of B_1 is distributed among the aldehyde proton and $H_2C=$ protons and the protons of the CH_3 group attached to the 12-C atom (signals 1, 2, and 4 in Figure 3). In I, this polarization manifests itself as the signal of the protons of two CH_3 groups. Hence, the amplitude ratio of the intensities of signal 1, multiplied by a factor of 6, and signal 5 corresponds to the ratio of the rate constants of the disproportionation (k_d) and recombination (k_r) of the alkyl−acyl biradicals, which is estimated at 5.8.

Emission signals 6 and 7 (see Figure 3 and Table 2) point to the presence of a competitive process of sorting RPs by nuclear spin projections. In our case, it is decarbonylation which induces polarizations of opposite signs in the recombination products of the consecutive biradicals.

Since the bisalkyl biradical has twice as many β-protons as the acyl−alkyl biradical, one could expect a 2-fold increase in the disproportionation-to-recombination ratio for the bisalkyl biradical, the change in the activation barrier being disregarded. The intensity ratio of the signals of the methyl protons of IV and V (signals 6 and 7) allows one to estimate the rate constant ratio of the disproportionation and recombination of the bisalkyl biradical at $k_d/k_r \approx 14$.

We have determined that at room temperature and at $t = 1$ μs, the evolution of the biradicals is complete and the nuclear polarization reaches a stationary value. It is interesting that at

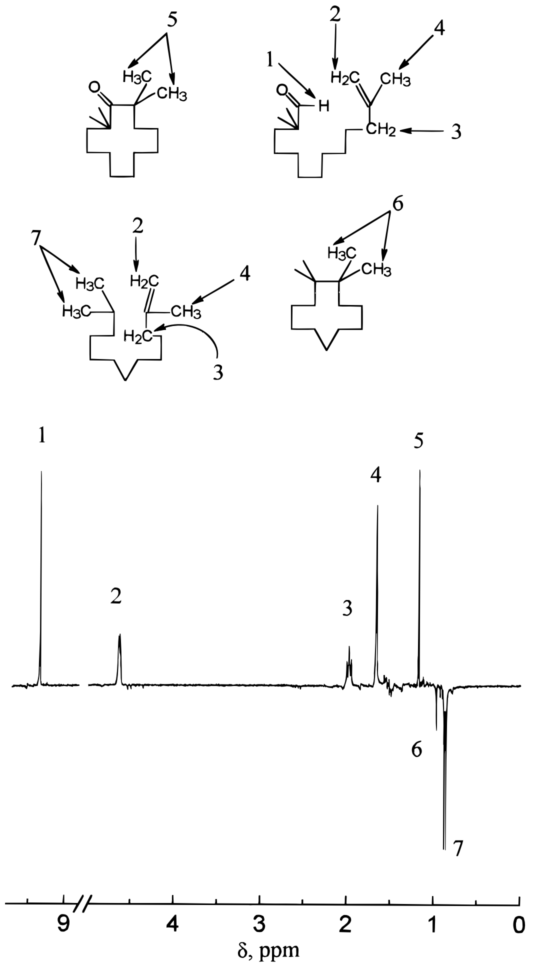


Figure 3. ^{1}H CIDNP spectrum obtained during the photolysis of 2,2,12,12-tetramethylcyclododecanone in cyclohexane-d_{12} at the magnetic field 7 T.

TABLE 2: ^{1}H Chemical Shifts and CIDNP Signs at High Magnetic Fields for the Producsts of the Photolysis of 2,2,12,12-Tetramethylcyclododecanone in Cyclohexane-d_{12} (A, Enhanced Absorption; E, Emission)

no.	nucleus	compd and its no. in Scheme 1	chem shift, ppm	CIDNP sign
1	C(=O)H	II	9.34	A
2	=CH$_2$	II	4.63	A
		V	4.63	E
3	11-CH$_2$	II	1.96	A
	3-CH$_2$	V	1.96	E
4	12-CH$_3$	II	1.66	A
	2-CH$_3$	V	1.66	E
5	CH$_3$	I	1.18	A
6	CH$_3$	IV[a]	0.97	E
7	(C**H**$_3$)$_2$CH	V	0.86	E

[a] 1,1,2,2-Tetramethylcycloundecane.

$t = 1$ μs, the total (all over the spectrum) net nuclear polarization of all spectral lines is non-zero, although the S−T$_0$ approximation, which ignores the relaxation processes in biradicals, implies the total compensation of the polarization. However, in our previous work,[20] we also observed a non-zero stationary nuclear polarization (about one-fourth of the maximum value) of the alkyl−acyl biradicals arising in the photolytic reactions of unsubstituted cyclic ketones. To the best of our knowledge, there is as yet no plausible explanation for this phenomenon. Perhaps it is associated with the nuclear paramagnetic relaxation; however, the typical times of nuclear relaxation in radicals are considerably longer (10^{-4}−10^{-3} s[35]) than the observed lifetimes of the biradicals. In order to fit the calculations to the experimental kinetic data, we had to limit the biradical lifetime τ_0 by including the non-zero scavenging rate constant k_{sc} into the calculations.[20] The best fit was obtained at $k_{sc} = \tau_0^{-1} = 10^6$ s^{-1}.[20]

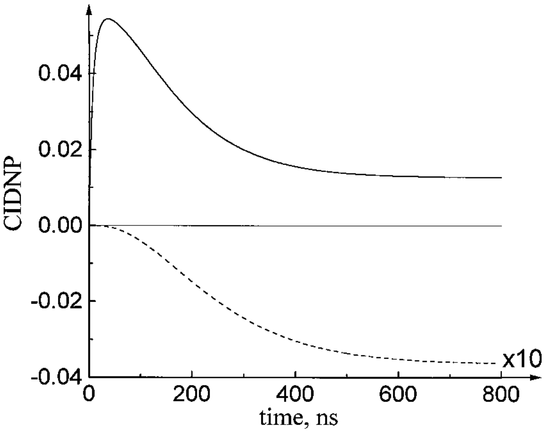


Figure 4. Calculated ^{1}H CIDNP kinetics for the recombination products of the alkyl−acyl biradicals (solid line) and bisalkyl biradicals (dashed line) arising in the photolysis of 2,2,12,12-tetramethylcyclododecanone. Calculation parameters: $k_r = 1 \times 10^{11}$ s^{-1}, $k_{sc} = 1.3 \times 10^6$ s^{-1}, $k_{soc} = 10^7$ s^{-1}, $J_0 = 10^{10}$ s^{-1}, α = 2.136 ($J = J_0 e^{-\alpha r}$), $D = 10^{-5}$ cm^2/s, $\tau_u = 10^{-12}$ s, $\tau_c = 10^{-11}$ s.

The kinetics of CIDNP generation in different products could provide direct evidence for the presence of the consecutive biradicals. To detect the CIDNP kinetics, we used the rf pulses of the half-width 150 ns. Since in biradicals the geminate evolution takes hundreds of nanoseconds, the observed CIDNP kinetics is a convolution of the rf pulse with the real CIDNP kinetics. Thus, we used the calculated CIDNP kinetics to determine the theoretical dependence of the signal intensity on the delay between the laser and rf pulses, taking into account the shape of the rf pulse.[36]

Figure 4 (solid line) shows the calculated CIDNP kinetics for the recombination products of the alkyl−acyl biradicals. The calculation details are given in section 3, and the parameters are listed in the caption to Figure 4. From the viewpoint of CIDNP generation, the eight protons of the alkyl end are equivalent. After recombination or disproportionation, the polarization of these protons is transferred to products I and II. Therefore, protons of I and II have similar behavior of CIDNP kinetics, which differs only in absolute magnitude, depending on the number of protons contributing to an individual line. The analysis of the experimental data confirms this suggestion.

The CIDNP kinetics of the recombination products of the alkyl−acyl biradicals calculated taking into account the convolution procedure (vide supra) and the corresponding experimental points are shown in Figure 5a. The CIDNP kinetics has a maximum and a non-zero stationary value. To obtain the non-zero stationary polarization for the calculated curve, we should take into account the scavenging reaction with the rate constant k_{sc}. The value $k_{sc} = 1.3 \times 10^6$ s^{-1} gives the best fit to the experimental data. It should be noted that this k_{sc} is different from the decarbonylation rate constant because of the incomplete compensation of the net polarization (vide supra). In the photolysis of tetramethylcyclododecanone, $k_{sc} = k_{co} + \tau_0^{-1}$, where k_{co} is the decarbonylation rate constant. For $\tau_0^{-1} = 10^6$ s^{-1}, the rough estimate of k_{co} is 3×10^5 s^{-1}. This value lies within the range of the decarbonylation rate constants for the pivaloyl radical in various solvents.[37]

In the bisalkyl biradicals resulting from decarbonylation, no net nuclear polarization is generated ($\Delta g = 0$). Hence, the net polarization of the products of the bisalkyl biradicals is formed

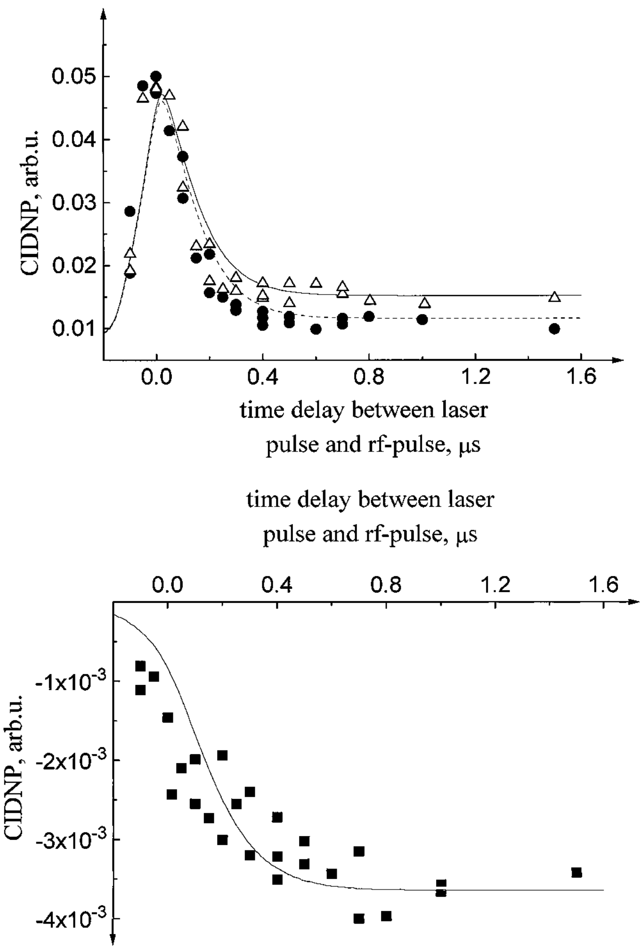


Figure 5. Effect of the rf pulse on the calculated ^{1}H CIDNP kinetics (see Figure 4) for the recombination products of alkyl−acyl (a, top, solid line) and bisalkyl biradicals (b, bottom) and their superposition (a, top, dashed line). Experimental points: △, for signal 1 (aldehyde proton of II); ●, for signal 4 (13-CH$_3$ protons of II and 2-CH$_3$ protons of V); ■, for signal 7 ((C**H**$_3$)$_2$CH protons of V).

in the primary alkyl−acyl biradical and then, on decarbonylation, is transferred to the secondary biradicals. The CIDNP kinetics of the recombination products of the bisalkyl biradicals can be calculated using the simplified reaction scheme

$$\begin{tikzcd} \mathrm{B}_1 \arrow[r, "k_1(I_z)"] \arrow[d, "k_{\mathrm{co}}"] & \mathrm{Pr}_1 \\ \mathrm{B}_2 \arrow[r, "k_2"] & \mathrm{Pr}_2 \end{tikzcd}$$

where Pr$_1$ and Pr$_2$ are the sets of the products of acyl−alkyl (B$_1$) and bisalkyl (B$_2$) biradicals, respectively.

The polarization of the products of the bisalkyl biradicals arises due to differences in k_1 of different nuclear spin projections I_z of biradicals B$_1$. Taking this into account in integrating the kinetic equations allows one to obtain the CIDNP kinetics of the products of the geminate recombination of B$_2$,

$$P_0(t) = \sum_{I_z} \frac{W(I_z) I_z k_{\mathrm{co}} k_2}{k_2 - k_{\mathrm{co}} - k_1(I_z)} \times \left[\frac{1}{k_{\mathrm{co}} + k_1(I_z)}(1 - \mathrm{e}^{-(k_{\mathrm{co}}+k_1(I_z))t}) - \frac{1}{k_2}(1 - \mathrm{e}^{-k_2 t})\right] \quad (7)$$

Here $W(I_z)$ is the statistical weight for a given nuclear spin projection I_z.

The CIDNP kinetics calculated by this method is shown in Figure 4 (dotted line). For I_z from 4 to −4, the values of $k_1(I_z)$ were calculated by the procedure described in section 3. Since there is no net polarization induced in B$_2$, k_2 was assumed to be equal to the average value of $k_1(I_z)$ for all I_z. The width and shape of the rf pulse were taken into account by deconvolution[35] of the calculated CIDNP kinetics for the recombination products of the bisalkyl biradical. The resulting curve and the corresponding experimental points are shown in Figure 5b.

Summarizing the time-resolved CIDNP results, we can conclude that the observed signals can be divided into three groups.

1. The polarization of starting ketone I, as well as that of aldehyde II, is formed only in the primary biradicals, and signals 1 and 5 correspond only to the recombination products of the primary biradicals. Thus, the CIDNP kinetics of the products is typical of the alkyl−acyl biradicals (Figure 5a).

2. Signals 6 and 7 correspond only to the recombination products of the secondary biradicals. The amplitude of these signals increases monotonically and reaches a stationary value (Figure 5b).

3. In products II and V, the chemical shifts of the protons of the unsaturated end coincide (see Table 2). Therefore, at short times, at which the contribution of decarbonylation is insignificant, the kinetic behavior of signals 2, 3, and 4 is similar to that of signals 1 and 5. At long times, both the positively polarized protons of II and the negatively polarized protons of V contribute to signals 2, 3, and 4. Therefore, for these lines, the stationary value of CIDNP is lower, relative to the maximum, than the corresponding value for lines 1 and 5 (Figure 5a).

5. Conclusions

The photoexcitation of 2,2,12,12-tetramethylcyclododecanone gives rise to the primary biradicals, which undergo a slow chemical transformation (decarbonylation) to yield the secondary biradicals. It is shown that the decarbonylation reaction can serve as a competitive process of sorting RPs by nuclear spin projections at high magnetic fields. The latter manifests itself in different signs of ^{1}H and ^{13}C CIDNP as well as in the kinetic behavior of the proton polarization of the recombination (disproportionation) products of the consecutive biradicals. The ^{1}H CIDNP field dependence confirms the assumption that the photolysis of the ketone under study involves two types of biradicals with different chain lengths. The polarized signals of the starting ketone indicate that the recombination of the primary biradicals is rather effective.

It appears to be interesting to compare the results reported in this work with the data on the CIDNP of the biradicals subject to a fast chemical transformation that competes with the singlet−triplet evolution, where the CIDNP memory effect might be expected. This work is now in progress.

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