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Study of Consecutive Biradicals from 2-Hydroxy-2,12-dimethylcyclododecanone by TR-CIDNP, TREPR, and Laser Flash Photolysis

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Several time-resolved spectroscopic techniques (^{1}H CIDNP, time-resolved EPR, and nanosecond laser flash photolysis) have been used to investigate geminate reactions of consecutive biradicals generated from photolysis of 2-hydroxy-2,12-dimethylcyclododecanone (**1**). It is shown that the primary photochemical process is Norrish type I cleavage, yielding an acyl−ketyl biradical, which is transformed to an alkyl−ketyl biradical via decarbonylation. The rate constant for decarbonylation, estimated by theoretical modeling of the TR-CIDNP kinetics, is $(4.2 \pm 1.0) \times 10^5$ s^{-1}. The calculations are based on the numerical solution of the stochastic Liouville equation for the Fourier transform of the biradical spin density matrix. The lifetime of the acyl−ketyl biradical ($\tau = 67 \pm 8$ ns) has been measured using laser flash photolysis. The distribution of reaction products in the photolysis of **1**, including recombination to the starting ketone, was determined from the CIDNP amplitude and kinetics. The reaction products include unstable compounds containing enol functional groups, which are transformed to the keto form during the dark reaction of tautomerization.

Introduction

In recent years, the physical and chemical properties of biradicals generated in the photolysis of cyclic aliphatic ketones have been the focus of many investigations using time-resolved magnetic resonance techniques. Many experiments on biradicals have involved the time-resolved (direct detection) electron paramagnetic resonance (TREPR) method, which allows for reliable identification of paramagnetic intermediates arising from photolysis,[1−5] and the laser flash photolysis method, which is useful for measuring biradical lifetimes.[6−8] However, these methods provide little information about the chemical and spin mechanisms of biradical decay, or about the formation of the final products from photolysis. The results of chemical analyses of reaction products can sometimes be unreliable because of the possibility of slow secondary dark reactions (e.g., keto−enol tautomerization) and secondary photochemical reactions of the products.

We have previously shown that it is possible to follow the chemical reactions of biradicals by analyzing the kinetics of chemically induced dynamic nuclear spin polarization (CIDNP) of the reaction products.[9] Time-resolved CIDNP (TR-CIDNP) allows one to detect the kinetics of polarized reaction products in the submicrosecond time domain. The high enhancement factors of CIDNP make the measurements possible at very low degrees of conversion, which eliminates the possibility of secondary chemical reactions. The kinetics of CIDNP in the products of biradical reactions after the photolysis of cyclic aliphatic ketones have been studied in two previous papers from one of our laboratories.[9,10] In that work it was shown that the application of this technique is beneficial in the case where primary biradicals B_1 transform to secondary biradicals B_2, e.g. by decarbonylation.[9] Depending on the rate of this reaction, the sign of the nuclear polarization of the products of B_2 either coincides with the sign of the nuclear polarization of the products of B_1 (this is the so-called CIDNP “memory effect” [11,12]) or is opposite to it (i.e., similar to the sign of the CIDNP in the escape products). These two cases correspond to fast and slow transformation rates between B_1 and B_2, respectively.

In the CIDNP kinetics of the geminate products formed after photolysis of 2,2,12,12-tetramethylcyclododecanone,[9] we were able to experimentally separate the contributions to the polarization of the initial acyl−alkyl biradical and the secondary bis(alkyl) biradical. We determined the decarbonylation rate constant and revealed all steps of chemical transformations of the consecutive biradicals, including the recombination of the primary alkyl−acyl biradical to the starting ketone. In this work, we use the TR-CIDNP method in combination with TREPR and laser flash photolysis (LFP) to continue our study of “consecutive biradicals”, in particular those produced from 2-hydroxy-2,12-dimethylcyclododecanone (**1**), which has two α-methyl substituents and an additional α-hydroxyl. Hydroxylated biradicals are of interest to us for several reasons. For example, in mono radicals produced from linear α-hydroxyketones, electron−nuclear cross relaxation effects[12] and solvent-dependent decarbonylation rates[13] have been observed. We are interested in whether similar effects are observed when the radical centers are covalently linked, and in making a comparison between alkylated and hydroxylated biradical spin and chain dynamics. Decarbonylation is interesting in these systems in general because they are an order of magnitude faster at room temperature than their corresponding alkyl analogues.

Unlike tetramethylcyclododecanone, **1** has α-C−C bonds which are not equivalent with respect to the Norrish I cleavage reaction. This can lead to the formation of two types of initial biradical, depending on the direction of cleavage. Biradical formation is followed by either recombination, O−H or C−H disproportionation through different channels, or decarbonylation yielding the secondary alkyl−ketyl biradical. In this paper we describe the detailed experimental and theoretical analysis of the CIDNP kinetics of the geminate products of consecutive

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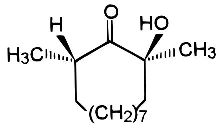
biradicals that arise in the photolysis of **1** at a magnetic field of 7 T in methanol-d_4 and acetonitrile-d_3. On the basis of the TR-CIDNP results, we propose a mechanism for this process and the distribution of products from this photolysis. The TREPR and LFP techniques have been used where necessary to support our kinetic model and structural analysis.

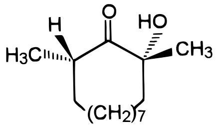
Experimental Section

The general principles of the time-resolved CIDNP method have been described in a review by Closs and Redwine.[14] A detailed description of our experimental apparatus is given in a previous paper.[9] A sample sealed in a standard NMR Pyrex ampule was irradiated by an excimer laser (wavelength 308 nm, pulse energy 120 mJ) in the probe of an MSL-300 Bruker NMR spectrometer. The probe of the NMR spectrometer was specially adapted for TR-CIDNP experiments. Instead of the standard saddle-shaped coil, a home-made double-frequency resonator with a working frequency of 300 MHz and a lock frequency of 46 MHz was used. The time resolution was increased by damping the Q-factor of the resonator at 300 MHz during the detecting rf-pulse application, which resulted in decrease of the rf-pulse rise time.[14] The amplitude of the rf pulse was increased by a homemade 1 kW power amplifier. Under these conditions, the duration of the $\pi/2$ pulse was 1.9 μs. The kinetics were measured using detection pulses with half-widths of 150 ns, which corresponds to a rotation of the magnetization vector by 7°. The setups used in the X-band TREPR[15] and laser flash photolysis[16] experiments have also been described in previous papers. The solvents CD_3OD and CD_3CN from Izotop (Russia) and CH_3OH from Reakhim (Russia) were used. The optical density of the solutions in all TR-CIDNP experiments was 0.6 Prior to irradiation, the samples were bubbled with argon gas for 5 min. In the TREPR experiment, nitrogen gas was bubbled through the flowing samples for 10 min prior to and throughout the experiments.

Synthesis of compound **1** was accomplished as follows:[17] Cyclododecanone (Aldrich) was methylated on opposite sides of the ketone using standard enolate chemistry (sequential addition of lithium diisopropyl amide (LDA) and methyl iodide in THF at −40 °C). The enol ether of 2,12-dimethylcyclododecanone was made with 1.1 equiv of LDA and 1.1 equiv of chlorotrimethylsilane. The mixture was allowed to stir overnight. Workup with ether and saturated sodium bicarbonate solution yielded a yellow oil after evaporation of the solvent. To epoxidize the enol ether, dichloromethane and solid sodium bicarbonate were added to the crude material. The flask was placed in an ice bath and 1.5 equiv of 3-chloroperoxybenzoic acid in dichloromethane was added dropwise. After stirring for 1 h, a small amount of sodium sulfite solution was added. Workup with 2 M sodium hydroxide and dichloromethane yielded another yellow oil. Addition of 5:1 methanol to 10% hydrochloric acid caused the solution to become slightly cloudy. After 30 min of stirring, the methanol was stripped to yield a cloudy oil. Extraction with ether and saturated sodium bicarbonate solution gave a clear oil from which crystals formed immediately. Recrystallization from hexanes yielded white crystals of 2-hydroxy-2,12-dimethylcyclododecanone, **1**. This compound can exist in the form of two stereoisomers, *cis* and *trans*:



cis



trans

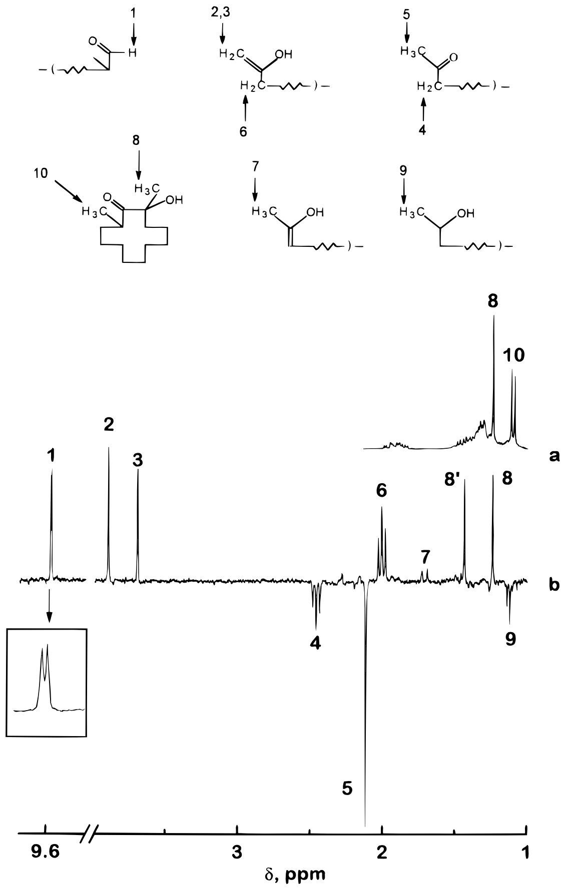


Figure 1. (a) “Dark” ^{1}H NMR spectrum of **I** in CD_3OD. (b) ^{1}H CIDNP spectrum during the photolysis of **1** in CD_3OD at the delay time between laser and rf pulses of 1 μs. The duration of rf pulse was 2 μs.

X-ray analysis of the crystals of **1** indicated that the synthetic procedure described above yields only *cis* isomer of **1**.

Characterization data (^{1}H and ^{13}C NMR, MS, UV/vis, IR) are available upon request from the corresponding authors.

Results and Discussion

For α-substituted cyclic aliphatic ketones, it is well-known that the primary photochemical process is the cleavage of the α-C−C bond from the triplet excited state. Since **1** is asymmetric with respect to α-cleavage, the latter can result in the formation of two types of biradicals B_1 and B_1':

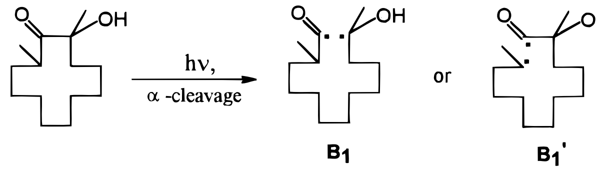


Figure 2 shows room temperature X-band TREPR spectra obtained at a delay time of 0.1 μs after laser excitation (308 nm) of **1** in methanol. Almost the same spectra were recorded in acetonitrile and methylcyclohexane. The shape of the spectra and their broad line widths indicate that the signal carrier in the spectrum is a biradical with an acyl radical center.[2,15] However, from the spectral appearance we cannot conclude whether the second biradical moiety is a ketyl ($COHCH_3$) radical center or an alkyl ($CHCH_3$) one.

The EPR signal disappears completely within a few hundred nanoseconds after the laser flash, which, for reasons to be detailed below, is also consistent with assignment to the biradical

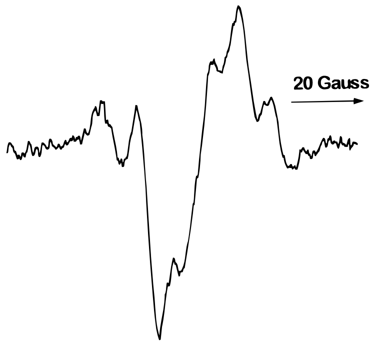


Figure 2. X-band (9.46 GHz) TREPR spectra obtained during the photolysis of 0.1 M **1** in methanol at 0.1 μs delay time after the laser pulse.

with the acyl radical center. The TREPR spectrum observed at a delay time of 0.3 μs has the same shape, but much worse signal to noise ratio. This means that the decay rate constant is determined by triplet−singlet transitions followed by recombination from the singlet state. Initially, three equally populated triplet sublevels decay with different rate constants. Efficient S−T$_0$ mixing due to hyperfine interaction (hfi), which typically is on the order of 10^8 s^{-1}, leads to a very fast decay of the T$_0$ population. The decay of the T$_+$ and T$_-$ sublevels can occur by correlated dipole−dipole and uncorrelated spin relaxation processes, as discussed by de Kanter et al.[19] However, the relaxation rate constants in such biradicals are usually a little bit slower than the decay rate observed here. Typically they are in the range of a few microseconds.[2] Spin−orbit coupling (SOC) is another possible mechanism which can provide a very efficient channel of S−T mixing, and the rate constant for the biradicals with an acyl radical center can be as high as 10^7 s^{-1}.[6−8]

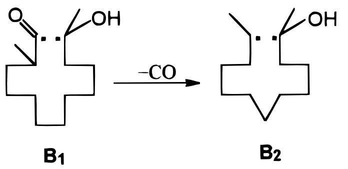
The CIDNP observed in the products of the biradical reactions arises due to a difference in the *g* factors of the radical centers and the hyperfine interaction of each unpaired electron with the neighboring nuclei. The biradicals are characterized by different spin density distributions, which makes the CIDNP spectrum sensitive to the nature of the paramagnetic intermediates. Because these biradicals are structurally similar to their corresponding monoradicals, we can easily estimate several magnetic resonance parameters of B$_1$ and B$_1$′. For both biradicals,[18] the *g* factor of the acyl fragment is 2.0008; for the ketyl end of B$_1$, $g = 2.0032$, $A(\mathrm{b,CH_3}) = +1.9$ mT, and $A(\mathrm{b,CH_2}) = +1.7$ mT; for the alkyl end of B$_1$′, $g = 2.0026$, $A(\mathrm{a,H}) = -2,.1$ mT, and $A(\mathrm{b,CH_3}) = +2.4$ mT, $A(\mathrm{b,CH_2}) = +2.7$ mT.

In case of recombination of biradicals B$_1$ and B$_1$′, the initial compound would be restored. However, in the recombination of B$_1$, the 2-CH$_3$ group protons should be polarized, while in the case of B$_1$′, the polarization should be generated in the 12-CH$_3$ group protons and in the lone α-proton. In the disproportionation products of the biradicals, the polarized aldehyde proton should appear as a doublet for B$_1$ (due to the interaction with the α-proton) and as a singlet for B$_1$′.

The dark ^{1}H NMR spectrum of **1** in CD$_3$OD is shown in Figure 1a. Figure 1b shows the ^{1}H CIDNP spectrum obtained during the photolysis of **1** in CD$_3$OD. The latter spectrum contains no equilibrium signals, because each laser pulse was preceded by a series of presaturating rf pulses. It can be seen that in our CIDNP spectrum for the starting compound, the polarized signal is that of the 2-CD$_3$ group (signal 8). The weak-field region of the spectrum contains signal 1 (doublet), which corresponds to the aldehyde proton. This testifies unambiguously that photolysis of the starting ketone yields only the B$_1$ biradical. It indicates that the formation of acyl−ketyl biradical from the triplet state of the initial ketone is energetically more favorable than the formation of acyl−alkyl biradical.

In the CIDNP spectrum shown in Figure 1b, the initial compound manifests itself by signals due to the 2-CH$_3$ groups (8 and 8′), which correspond to the stereoisomers described in the Experimental Section. The dark spectrum of **1** (Figure 1a) exhibits only the signals of the *cis* isomer. The approximately equal intensities of signals 8 and 8′ suggest that the recombination of the biradicals is not stereospecific, which is not unexpected.

The α-substituents accelerate the decarbonylation process.[20] In this case, the formation of the secondary alkyl−ketyl biradical B$_2$ results:



The decarbonylation process should be reflected in the kinetics and in the sign (emissive or absorptive) of the CIDNP generated in the products of the biradical reactions. Therefore, TR-CIDNP allows the identification of all chemical processes that occur during the photolysis of the compound under study. Below we present a qualitative description of the CIDNP kinetics in the geminate recombination of these biradicals in the presence of spin-independent reactions concurrent with the geminate processes.

In strong external magnetic fields, the CIDNP kinetics of “long” (>C$_{10}$) biradicals are adequately described in terms of the S−T$_0$ approximation. The triplet biradicals generated in the photochemical reaction are divided into nuclear-spin subensembles with different rates of singlet to triplet conversion. Since in biradicals the separation of the radical centers by diffusion is not possible, the initial process is that “fast” and then “slow” nuclear subensembles are transferred to the singlet state and yield diamagnetic products. In this case, the CIDNP kinetic curve reaches a maximum and vanishes and the sign of the nuclear polarization will be that predicted by Kaptein’s rules[21] for the geminate products. From the magnetic resonance parameters of the acyl−ketyl biradical B$_1$ given above and application of Kaptein’s rules for a triplet precursor, a positive Δg, and a positive hyperfine coupling constant, the products formed from the geminate reactions should exhibit positive nuclear polarization, i.e., enhanced absorption.

If biradical B$_2$ results from a spin-invariant chemical transformation of biradical B$_1$ during its geminate evolution, some nuclear-spin subensembles of the biradical B$_1$ will not appear in its products. For the subensembles of B$_1$ with lower rates of singlet−triplet conversion, the probability of chemical transformations to B$_2$ is higher. Therefore, for biradical B$_1$, chemical transformation plays a role similar to that of a scavenging reaction. This reaction removes the biradicals with low rates of S−T conversion from geminate reactions. The manifestation of this scavenging effect is the appearance of nonzero stationary CIDNP in the products. An increase in the scavenging rate first increases the stationary value of the CIDNP with respect to the maximum. At a certain scavenging rate, the CIDNP kinetic curve loses its maximum and becomes monotonic in time with no extrema. Any further increase in the scavenging rate decreases the amplitude of the geminate CIDNP, with the kinetic curve retaining the same behavior. The dependence of the stationary CIDNP amplitude on the scavenging rate k_{sc} is expressed through the Laplace transform for the CIDNP kinetics calculated in the absence of scavengers.[22]

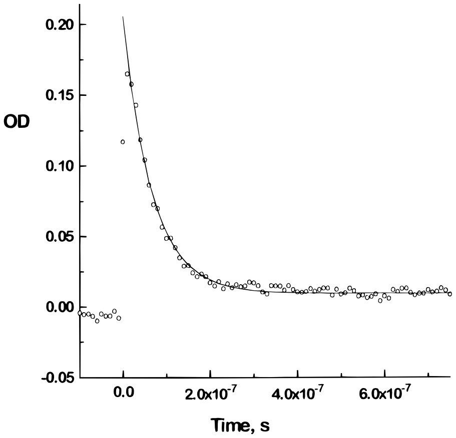


Figure 3. Transient absorption kinetics detected during the photolysis of 2.2×10^{-2} M **I** in methanol at zero magnetic field. Solid line, exponential fit with the characteristic time 67 ns.

As mentioned above, biradical B_2 is generated with spin states that have slow S$-$T conversion, which will lead to net nuclear polarization of a sign that is opposite to that of the geminate polarization. In the case reported here, the chemical transformation is decarbonylation, to yield biradical B_2. This biradical has a small Δg and therefore no significant additional net nuclear polarization is induced. Also, the initial electron spin multiplicity of the secondary biradical is not that of a pure triplet. Hence, although the products of the secondary biradicals are geminate, their nuclear polarization should be emissive, which corresponds to a sign of polarization predicted for "escaped" products. The presence of emissive signals in the CIDNP spectrum (Figure 1b) suggests that decarbonylation is fast enough in these biradicals to be a spin-sorting process.

Figure 3 shows the transient absorption kinetics detected during the photolysis of 2.2×10^{-2} M solution of **1** in methanol. The kinetics depend weakly on both the magnetic field strength and on the initial concentration of the biradicals.[24] This suggests rapid (<10 ns) generation of the acyl$-$ketyl biradicals. They decay exponentially with a rate constant of 1.5×10^{7} s^{-1}. The LFP method allows an exact determination of the biradical lifetimes but gives no information on the channels of biradical decay. At the same time, by analyzing the CIDNP amplitude and kinetics, we can quantitatively determine the partitioning of the products formed from the biradical reactions.

In addition to recombination, biradicals B_1 and B_2 can undergo O$-$H or C$-$H disproportionation by either (1) abstraction of the b-hydrogen atom from the ketyl radical or (2) addition of the H atom to the ketyl radical center (abstraction of the hydrogen atom attached to the hydrocarbon radical b-carbon). The latter of these two pathways results in the formation of products in which the "ketone", two types of "enol", and "alcohol" functional groups are linked by a polymethylene chain to the second functional group corresponding to a certain type of disproportionation (Table 1). Since the polymethylene chain is very long, the "ketone", "enol", and "alcohol" protons in the product of biradicals B_1 and B_2 exhibit the same chemical shifts in their NMR spectra. Table 2 shows the chemical shifts and CIDNP signs for the different protons. We emphasize here that contributions from B_1 and B_2 reaction products to the CIDNP signals can be separated only in the time-resolved experiment.

Figure 4 shows the CIDNP kinetics for different protons. The CIDNP kinetics of the aldehyde and enol protons (Figure 4a) practically coincide. The "aldehyde" fragment arises in the disproportionation of B_1, while the "enol" fragment can appear due to products formed from both B_1 and B_2. However, if this was the case, both the positively polarized protons of the B_1 product (at the initial times) and the negatively polarized protons of the B_2 product (at longer times) would make their contributions to the nuclear polarization of enol protons. In this case, for the enol protons, the value of the stationary CIDNP would be lower relative to its maximum than the corresponding value for the aldehyde protons. This is similar to what has been observed in the CIDNP study of products from photolysis of 2,2,12,12-tetramethylcyclododecanone.[9] The coinciding CIDNP kinetics of the aldehyde and enol protons indicate that the C$-$H disproportionation occurs mainly in the primary biradical. Changing the solvent from CD_3OD to CD_3CN does not significantly affect the CIDNP kinetics. This fact is in agreement with our TREPR results: EPR spectra of B_1 in these two solvents were almost the same.

In our time-resolved experiments, the CIDNP of the ketone (except the starting ketone) and alcohol group protons were always in emissive phase. The polarization values monotonically increased in time and reached stationary values (Figure 4b). This suggests that O$-$H disproportionation reactions occur mainly in the secondary biradical. The NMR spectra of the reaction products exhibit signals corresponding to linear mol-

TABLE 1: Products of Consecutive Biradicals Arising in the Photolysis of 2-Hydroxy-2,12-dimethylcyclododecanone

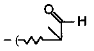
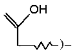
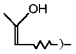
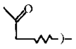
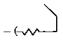
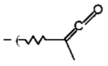
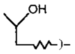
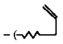
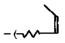
Products from biradical B_1		▨
▨	Products from biradical B_2	
Acyl moiety	Ketyl moiety	Alkyl moiety
 "aldehyde" moiety	 "enol" moiety  "enol" moiety  "ketone" moiety	 "alkane" moiety
 "ketene" moiety	 "alcohol" moiety	 "alkene" moiety  "alkene" moiety

TABLE 2: ^{1}H Chemical Shifts and CIDNP Signs at High Magnetic Fields for the Products of the Photolysis of 2-Hydroxy-2,12-dimethylcyclododecanone

no.	nucleus	compd no. in Scheme 1	chemical shift, ppm solvent CD_3OD	chemical shift, ppm solvent CD_3CN	CIDNP sign[a]
1	C(=O)H	**II**, **III**	9.57	9.59	A
2	$=CH_2$	**II**	3.90	3.92	A
3			3.70	3.74	
4	$-$**CH$_2$**$-COCH_3$	**IV**	2.46	2.42	E
5	$-CH_2-$CO**CH$_3$**	**IV**	2.12	2.08	E
6	$-$**CH$_2$**$-C(OH)=CH_2$	**II**	2.01	2.03	A
7	$-CH=$	**III**	1.73	1.74	A
			1.69	1.70	A
8	2-CH_3	**I**	1.44	1.41	A
8′			1.24	1.21	A
9	(**CH$_3$**)CH(OH)$-$	**V**, **VI**	1.13	1.10	E
10	12-CH_3	**I**	1.10	1.06	

[a] A, enhanced absorption; E, emission.

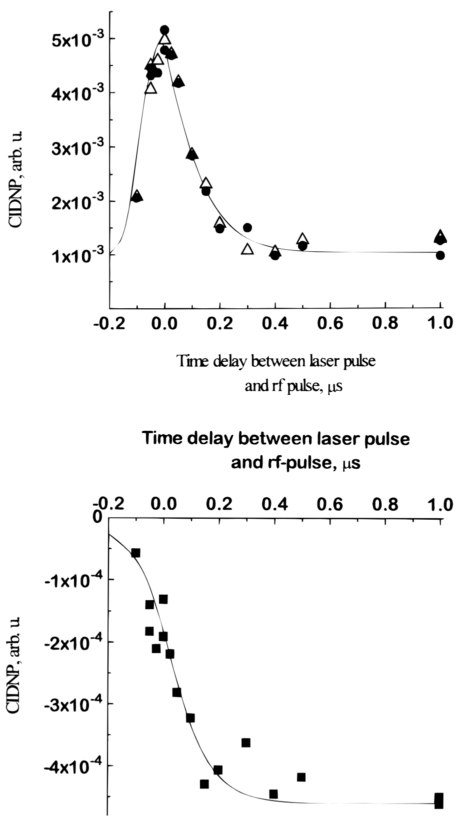
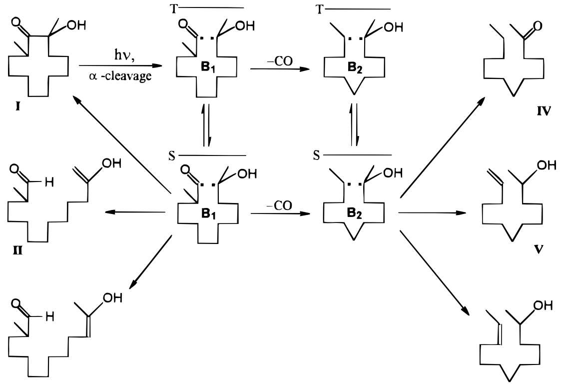


Figure 4. Effect of the rf pulse on the calculated ^{1}H CIDNP kinetics (solid lines) for the recombination products of acyl−ketyl (a, top) and alkyl−ketyl biradicals (b, bottom). Experimental points: (△) for signal 1 (aldehyde proton of II, III), (●) for signal 2 (alkene protons of II), (■) for signal 5 (H_3C-CO- protons of IV). Calculation parameters: $k_r = 1 \times 10^{11}$ s^{-1}, $k_{sc} = 1 \times 10^6$ s^{-1}, $k_{soc} = 10^7$ s^{-1}, $J_0 = -10^9$ mT, $\alpha = 2.136$ Å^{-1} ($J = J_0e^{-\alpha r}$), $D = 10^{-5}$ cm^2/s, $\tau_u = 10^{-12}$ s, $\tau_c = 10^{-11}$ s.

SCHEME 1



ecules with aldehyde, alcohol, and ketone functional groups, with the signals of the enol protons absent. This is accounted for by the fact that the enol molecules formed in the photolysis are transformed to the ketone ones via the dark reaction of keto−enol tautomerization, which occurs during the delay between the irradiation and detection. Thus, time-resolved CIDNP allows the detection of unstable products, which cannot be observed by other methods.

On the basis of the above data, we have proposed a scheme showing the radical reactions that occur upon photolysis of 2-hydroxy-2,12-dimethylcyclododecanone (Scheme 1; see also Table 2).

The CIDNP kinetics observed in the geminate recombination of the biradicals were modeled using the theoretical approach described elsewhere.[9,10] This approach is based on the de Kanter model for calculating the field dependencies of the stationary CIDNP of biradicals.[19] The model involves the numerical solution of the stochastic Liouville equation for the spin density matrix of a biradical:

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

where $\hat{L}$ is the Liouville operator, $\hat{R}$ is the relaxation matrix, $\hat{W}$ describes the dynamic behavior of the polymethylene chain, and $\hat{K}$ corresponds to the chemical reactions of the biradical.[19]

According to the de Kanter model, the distribution function of the biradical over the end-to-end distances is divided into segments of equal areas, and the diffusion jumps between these segments determine the relative motion of the radical centers. The spin and molecular dynamics are related through the exchange interaction which depends on the distance between the radical centers. To solve the kinetic problem, we substituted the Fourier transform of the density matrix $\tilde{\rho}(\omega) = \int_0^\infty \rho(t)\mathrm{e}^{-\mathrm{i}\omega t}\,\mathrm{d}t$ into eq 1 and obtained the stationary equation for $\tilde{\rho}(\omega)$:

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

The inverse Fourier transformation yields the time-dependent spin density matrix. Using this matrix, one can readily calculate the CIDNP kinetics. The details of such calculations have been described elsewhere.[9,10]

Because geminate evolution of the biradical spin states takes hundreds of nanoseconds, the experimental CIDNP kinetics are a convolution of the rf pulse and the CIDNP kinetics. Therefore, taking into account the shape of the rf pulse, we must calculate the CIDNP amplitude as a function of the delay between the laser pulse and the rf pulse.[24] This is shown in Figure 4a (solid line). The calculation parameters are listed in the figure caption. This kinetic curve has a characteristic maximum and a nonzero stationary value. A nonzero stationary value was also observed for the CIDNP of the products of the alkyl−acyl biradicals generated in the photolysis of unsubstituted cyclic aliphatic ketones.[9] In this system, the spin-sorting process is absent, and the $S-T_0$ mechanism should result in total compensation of the nuclear polarization at long times. The possible sources of the nonzero stationary CIDNP have been discussed earlier.[9] Presently, we can not give an exhaustive explanation of this effect. This is the subject of present research efforts.

For the geminate reactions of the biradical B_2, calculation of the CIDNP kinetics using the formalism of the spin density matrix[9,10] is rather cumbersome. Therefore, we used a simplified kinetic scheme:

$$\begin{tikzcd}
B_1 \arrow[r, "k_1(I_z)"] \arrow[d, "k_{CO}"] & Pr_1 \\
B_2 \arrow[r, "k_2"] & Pr_2
\end{tikzcd}$$

where Pr_1 and Pr_2 denote all the products formed before and after decarbonylation, respectively. This corresponds to the following system of differential equations:

$$\mathrm{d}[B_1]/\mathrm{d}t = -(k_1 + k_{CO})[B_1] \qquad (3)$$

$$\mathrm{d}[B_2]/\mathrm{d}t = k_{CO}[B_1] - k_2[B_2] \qquad (4)$$

$$\mathrm{d}[Pr_2]/\mathrm{d}t = k_2[B_2] \qquad (5)$$

TABLE 3: Product Distribution of the Photolysis of 2-Hydroxy-2,12-dimethylcyclododecanone

product	I	II	III	IV	V + VI
yield, %	28 ± 5	61 ± 5	7.7 ± 1	2.4 ± 0.5	0.9 ± 0.5

In the products formed from the biradical B_2, CIDNP is formed due to a difference in k_1 of different nuclear-spin subensembles. For the accumulation kinetics of product Pr_2 with particular nuclear spin projection I_z, we have

$$[\mathrm{Pr}_2](I_z) = [\mathrm{B}_1](t{=}0) \times \frac{W(I_z)k_{\mathrm{CO}}k_2}{k_2 - k_{\mathrm{CO}} - k_1(I_z)} \left[\frac{1}{k_{\mathrm{CO}} + k_1(I_z)}(1 - \mathrm{e}^{-(k_{\mathrm{CO}}+k_1(I_z))t}) - \frac{1}{k_2}(1 - \mathrm{e}^{-k_2 t})\right] \quad (6)$$

Here $W(I_z)$ is the statistical weight for a given nuclear spin projection I_z. Equation 6 leads to CIDNP kinetics in the products of B_2 given in eq 7:

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

The CIDNP kinetics are calculated for the CH_3 group protons of the ketyl end of biradical B_2. Using the calculation procedure described above for the time-dependent spin density matrix of B_1, values of $k_1(I_z)$ calculated for I_z from $-^3/_2$ to $^3/_2$ fall in the range from 1.36×10^7 to 1.46×10^7 s^{-1}, which is in good agreement with the results obtained by LFP (*vide supra*). For the products of B_2, the values of k_1 and k_2 determine the shape of the CIDNP kinetics, while the overall magnitude of the CIDNP is dependent on k_{CO}. The best fit of the experimental points to the calculated curve was obtained by variation of k_2 and was found to be 5×10^7 s^{-1}. The decarbonylation rate constant k_{CO} was varied to achieve the experimentally observed ratio of the polarizations of Pr_1 and Pr_2. From this procedure we estimate the rate constant of decarbonylation of B_1 to be 4.2×10^5 s^{-1}. It should be mentioned that decarbonylation is the minor channel of decay of B_1, which decays mainly via recombination/dispropotionation reactions. However, the decarbonylation rate constant is high enough to make contribution into the observed CIDNP signals.

Analysis of the CIDNP amplitude allows for quantitative estimation of the product distribution. The polarization of the CH_3 protons is generated in the primary biradical B_1 and then manifests itself as signals 1, 2, 3, 5, 7, 8, and 9 (Table 2). The signal intensity depends on the relative quantum yield of the polarized products and on the number of protons that make contributions to the individual line. Thus, normalizing the amplitude ratio of the CIDNP signals on the number of protons, we obtain the product distribution listed in Table 3.

Conclusion

Investigation of the photolysis of 2-hydroxy-2,12-dimethylcyclododecanone (**1**) by time-resolved magnetic resonance and optical methods has shown that this reaction occurs in two steps involving the generation of two consecutive biradicals: acyl−ketyl and alkyl−ketyl. The EPR and LFP methods allowed us to reliably detect only the acyl−ketyl biradicals and to estimate their lifetimes. Although time-resolved CIDNP is an indirect technique for detecting radical intermediates, its application to the investigation of the above photolytic reaction was very informative. The kinetics, amplitude, and sign of the CIDNP effects observed in these reaction products have allowed us to reliably establish the presence of two consecutive biradicals and have made it possible to follow their chemical transformations. On the basis of these data, we have proposed Scheme 1 for the overall reaction process, and we have determined the quantum yields of all the reaction products, including the unstable intermediates containing the enol group. It has been shown that for biradical B_1, the probability of recombination to the starting ketone is high. Also, the decarbonylation rate constant has been estimated. A subject of current investigation by similar methods is the photolysis of 2,12-dihydroxy-2,12-dimethylcyclododecanone, which should exhibit much faster decarbonylation in the initial acyl−ketyl biradical, and may lead to the observation of a CIDNP memory effect. A paper comparing mono- and dihydroxy biradical spin dynamics follows this paper.

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