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Laser Flash Photolysis and CIDNP Studies of 1-Naphthyl Acetate Photo-Fries Rearrangement

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The steady-state and time-resolved CIDNP and flash photolysis methods were used in a detailed study of the photo-Fries rearrangement of 1-naphthyl acetate (**I**) in acetonitrile and methanol. The main reaction channel is the decay of **I** through the excited singlet state with the quantum yields 0.17 ± 0.02 in acetonitrile and 0.42 ± 0.04 in methanol at room temperature. The absorption spectra of the naphthoxyl radical and triplet state of 1-naphthyl acetate were detected. The quantum yield of triplet was estimated as 0.4 ± 0.2 and 0.35 ± 0.17 in acetonitrile and methanol, respectively. It has been established that the triplet-born radical pairs make a main contribution to the CIDNP of the photo-Fries rearrangement products. The involvement in the process of two different triplet states of **I** was supposed. The main decay channel of the lowest triplet state is the triplet–triplet annihilation, while the CIDNP of photo-Fries rearrangement products results from the decay of the upper triplet state of **I** with a lifetime of a few nanoseconds. The kinetics of CIDNP formation in reaction products has been analyzed, and the rate constants of the rearrangement of the preceding intermediates at room temperature have been estimated.

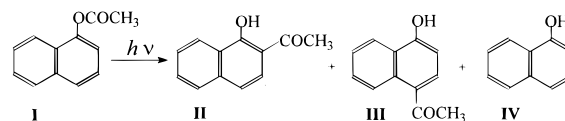
Introduction

The photo-Fries rearrangement was first discovered by Anderson and Reese¹ in 1960. Over the years this phenomenon has been extensively studied and has been observed not only in aryl esters^{1–5} but also in various aromatic compounds, including acetanilides,^{2,6–8} sulfonanilides,⁹ aryl sulfonates,^{2,10} carbamates,¹¹ sulfamates,¹² cinnamates,¹³ etc. Since the pioneering works,^{14,15} attempts have been made to elucidate the photo-Fries rearrangement mechanism. On the basis of the facts that product quantum yields are not affected by typical triplet quenchers^{2,3,7,8} and the triplet sensitization² is absent, some authors have assumed that the photo-Fries rearrangement occurs through the excited singlet state. This assumption has been supported by the analysis of the signs of CIDNP spectra^{16,17} detected during the photoirradiation of aryl esters. The appearance of the CIDNP effects has also revealed the radical mechanism of the photo-Fries rearrangement.^{16,17} However, some recent data indicate that in the case of phenylsulfamates and cinnamates the photo-Fries rearrangement occurs through the upper triplet states.^{12,13}

The photo-Fries rearrangement has much in common with such photochemical reactions as the photo-Claisen rearrangement^{18,19} and the β -cleavage of phenoxy ketones.^{20,21} The primary process of these phototransformations is the homolytic dissociation of the carbon–heteroatom bond, yielding a pair of free radicals. The recombining radicals form rearrangement products. A theoretical study of the homolytic photodissociation of the carbon–oxygen bond in R–O–Ph compounds has recently been performed by Grimme.²²

There are many works concerned with the investigation of the photo-Fries rearrangement; however, data on the rate

SCHEME 1



constants of elementary stages are lacking. The absorption of two intermediates was detected by Kalmus and Hercules²³ upon the pulse excitation of phenyl acetate. One of the intermediates was spectroscopically identified as the phenoxy radical. The other intermediate was assigned to cyclohexadienone which transforms to *o*-hydroxyacetophenone. The transformation of the cyclohexadienone intermediates to *o*- and *p*-hydroxy acetophenones has been recently described in detail by Arai.²⁴

This paper describes a detailed kinetic study of the phototransformation of 1-naphthyl acetate (**I**). It has been known that the irradiation of **I** in various solutions gives rise to the products typical of the photo-Fries rearrangement: 2-acetyl-1-naphthol (**II**), 4-acetyl-1-naphthol (**III**), and 1-naphthol (**IV**)^{2,4,5} (Scheme 1).

Nakagaki⁵ has detected the effect of an external magnetic field on the yield of product **II** for ¹³C-labeled 1-naphthyl acetate (¹³C=O). The value of the external magnetic effect (1.03 ± 0.01) suggests that the in-cage product originates from a singlet radical pair. The absorption of the intermediate in the laser excitation of **I** was attributed to the 1-naphthoxyl radical.⁵ However, this attribution seems to be justified insufficiently.

This work was aimed at determining the role of the excited singlet and triplet states in the photo-Fries rearrangement of compound **I** as well as at establishing the nature, spectral characteristics, and reactivity of the intermediates. To make the results more valid, we used complementary methods, including laser flash photolysis and steady-state and flash CIDNP.

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TABLE 1: Long-Wavelength Maxima in the Absorption Spectra (ν_{\max}), the Absorption Coefficients (ϵ_{\max}), and the Chemical Shifts of Methyl Protons (δ) in Methanol and the Melting Points of the Compounds under Study

	compound	ν_{\max} , cm ⁻¹	ϵ_{\max} , M ⁻¹ cm ⁻¹	δ , ppm	T_{m} , K
I	1-naphthyl acetate	31930	360	2.44	317–318
II	2-acetyl-1-naphthol	27180	5400	2.70	371–372
III	4-acetyl-1-naphthol	30470	11600	2.66	470–471
IV	1-naphthol	30820	3000		368–369

Experimental Section

Materials. 1-Naphthyl acetate from Chemapol was purified by sublimation in vacuo. Commercially available 1-naphthol was recrystallized from a water–ethanol mixture (1:9). 2-Acetyl- and 4-acetyl-1-naphthol needed for the identification of products were synthesized and isolated as described by Stoughton.²⁵

Ethanol and methanol were boiled over NaOH and distilled. Acetonitrile was repeatedly dried with P₂O₅ for an hour and distilled. CD₃CN and CD₃COD (99% enriched) from Isotope were used as received. 1,3-Pentadiene (piperylene) from Aldrich–Chemie, employed as a quencher, was distilled. Carbazole and acetophenone from Merck, used for sensitization, were additionally purified. The acetophenone was sublimated in vacuo. The carbazole was recrystallized from a water–ethanol mixture (3:7) two times. Phenanthrene from Merck was used as received.

Steady-State Photolysis. A high-pressure mercury lamp DRS-500 was used as a radiation source. The mercury line at 313 nm was isolated by a combination of UVS-2 and ZhS-3 glass filters. Absorption spectra were detected on a UV–vis Specord spectrophotometer. On irradiating samples at 160–300 K, 2-mm-thick quartz cells were inserted into the quartz tube of a Dewar flask with plane-parallel windows. Temperature was varied with a thermostable nitrogen jet, measured by a thermodiode, and maintained constant accurate to ± 0.5 K. Radiation-induced changes in absorption spectra were detected at room temperature. The concentration of dissolved oxygen was varied by passing oxygen or an argon–oxygen mixture (2:3) through solution for 20 min. Oxygen was removed from the solution by argon (99.99%) bubbling. Argon was passed through a piperylene-containing solution at low temperature (243 K) to not reduce the piperylene concentration.

The quantum yields of photolysis products **II–IV** were determined spectroscopically using available absorption spectra and absorption coefficients (Table 1). The photoreduction of anthraquinone in ethanol ($\phi = 0.98$)²⁶ was used as an actinometric reaction. The laser radiation intensity was measured by an IMO-2 joulemeter. On the sensitization of the photolysis of **I** by phenanthrene, carbazole, and acetophenone, the samples were irradiated by an LGI-21 nitrogen laser ($\lambda = 337$ nm).

Laser Flash Photolysis. The arrangement for time-resolved optical studies has been described elsewhere.²⁷ The solutions passing through the cell (inner dimensions 3×10 mm²) were irradiated by the light pulses of a Lambda Physik LPX 100 excimer laser (308 nm, pulse energy up to 100 mJ). The laser output was monitored by a Gentec ED-500 joulemeter, and the initial concentrations of excited species were determined as described earlier.²⁷ Oxygen was removed from all the solutions by purging with helium for 1 h prior to use. In the flash photolysis measurements, the optical density at 308 nm in the intersection of the laser and monitoring beams (2 mm) was kept below 0.2. All the data obtained by the flash photolysis technique and given below refer to a room temperature of 23 ± 1 °C.

CIDNP. Time-resolved CIDNP measurements were carried out on a Bruker AM-250 FT-NMR spectrometer (for details

TABLE 2: Quantum Yields of Products II–IV ($\phi_{\text{II}}-\phi_{\text{IV}}$) in the Photolysis of 1-Naphthyl Acetate (Measurement Accuracy $\pm 10\%$)

solvent	ϕ_{II}	ϕ_{III}	ϕ_{IV}	ϕ
acetonitrile	0.10	0.05	0.02	0.17
methanol	0.21	0.07	0.14	0.42

see ref 28). A sample inserted in a commercial cylindrical Pyrex ampule was irradiated inside the probehead of the spectrometer by an excimer laser beam (Lambda Physik EMG 101 MSC excimer laser, 308 nm, pulse energy up to 100 mJ). The light was supplied to the sample from the side of the ampule throughout an optical system consisting of two quartz lenses, a prism, and a light guide. Time-resolved CIDNP spectra were detected according to the conventional²⁹ pulse sequence: saturation–laser pulse–delay detection. The incident laser power was measured by the photodecomposition of dibenzyl ketone in benzene.^{28,30} It has been determined that about 20% of the inlet laser power reaches the sample.

To obtain the kinetics of CIDNP with the submicrosecond time resolution, short NMR detection pulses (500 ns, flip angle 20°) were used. The detection-pulse width and shape were taken into account by deconvolution procedure.³¹ In the CIDNP experiments, the optical density of the solutions at 308 nm was about 0.3 (optical pathway inside the sample tube about 4 mm). Since the piperylene content of the samples decreased under bubbling, the real concentration of piperylene was tested by the NMR spectra taken immediately prior to irradiation.

Steady-state CIDNP spectra were taken on a Bruker MSL-300 FT-NMR spectrometer by using the optical arrangement similar to that described above for the flash-CIDNP experiments. Samples were irradiated for 3 s at a repetition frequency of 7–10 Hz and NMR spectra were detected after the irradiation. CIDNP effects were determined as a difference between the spectra of irradiated and nonirradiated samples.

Quantum Chemical Calculations. Experimental data were interpreted by quantum chemical calculations using the MNDO,³² AM1,³³ and PM3³⁴ methods based on the modified MNDO-85 program.³⁵ The conventional Davidson–Fletcher–Powell procedure³⁶ was used to optimize the geometry. The geometry of radicals were determined by the restricted Hartree–Fock technique in a “half-electron” approximation.³⁷ The INDO³⁸ (UHF) method was applied to calculating the spin density distribution and the hyperfine interaction constants using the spin Hamiltonian program.³⁹

Results

1. Quantum Yields of Reaction Products. The UV irradiation of 1-naphthyl acetate (**I**) leads to the formation of three main reaction products: 2- and 4-acetyl derivatives of 1-naphthol (**II**, **III**) and unsubstituted 1-naphthol (**IV**)^{2,4,5} (see Scheme 1). Table 1 shows the positions of the absorption maxima and the absorption coefficients of the products at the wavelength maxima. These data were used in the spectroscopic analysis of the irradiated reaction mixture and in determining the quantum yields of the products.

It has been established that the quantum yields of the products formed in acetonitrile are independent of the concentration of **I** within 3×10^{-4} – 6×10^{-2} M. It is seen from Table 2 that the quantum yields of the products, in particular of 1-naphthol (**IV**), in methanol are essentially higher than those in acetonitrile. In both the solvents the yield of ortho product **II** is significantly higher than that of para product **III**. Attempts have been made^{3,12} to correlate the ratio of the ortho and para isomers arising in the photo-Fries rearrangement with the spin density

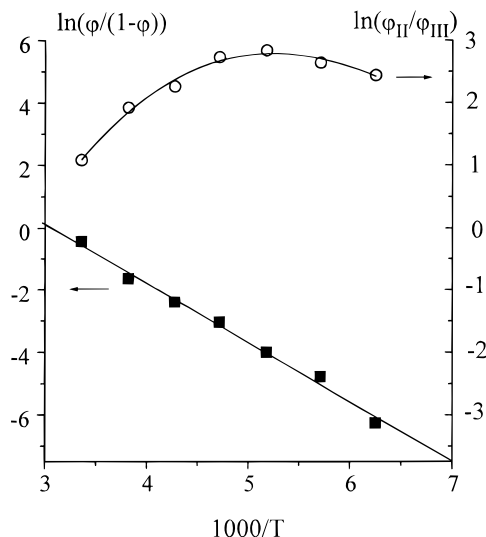


Figure 1. Temperature dependences of the quantum yield of 1-naphthyl acetate photo-Fries rearrangement (squares) and of the ratio of 2-acetyl and 4-acetyl-1-naphthol quantum yields (circles).

distribution in the aromatic radical. We have performed quantum chemical calculations of the spin density distribution in the naphthoxyl radical (see Appendix). The calculations show that position 4 has the highest spin density; however, the ortho product arises in a higher yield. Thus, in this case, the yield ratio of the products is not related to the spin density distribution but depends on solvent and temperature.

Our measurements show that the ratio of the quantum yields of products **II** and **III** ($\varphi_{\text{II}}/\varphi_{\text{III}}$) changes nonmonotonically with temperature (Figure 1). In ethanol, for instance, the value of the ratio first increases from 3 at room temperature to 15 at 200 K. With further decrease in temperature the value of the ratio $\varphi_{\text{II}}/\varphi_{\text{III}}$ slightly decreases. The quantum yields of the products decrease essentially with decreasing temperature. On the assumption that the 1-naphthyl acetate is not formed in cage during recombination and neglecting the radical escape from the cage, we obtain for the total quantum yield of the products

$$\varphi = k_{\text{dis}}/(k_{\text{dis}} + k_{\text{deac}})$$

where k_{dis} is the dissociation rate constant and k_{deac} is the rate constant of the deactivation of the excited state. From the above equation we derive the rate-constant ratio

$$k_{\text{dis}}/k_{\text{deac}} = \varphi/(1 - \varphi)$$

Figure 1 shows the temperature dependence of the quantum yield. It can be seen that the curve is well described by the Arrhenius law

$$\varphi/(1 - \varphi) = k_{\text{dis}}/k_{\text{deac}} = (5.8 \pm 0.3) \times \exp(-(1900 \pm 70)/T)$$

To study the dependence of the quantum yields on the exciting light intensity, the solutions were irradiated by the light of the mercury lamp ($\sim 1 \times 10^{16}$ quantum $\text{cm}^{-2} \text{s}^{-1}$) or by the pulsed light of the excimer laser (4.3×10^{24} quantum $\text{cm}^{-2} \text{s}^{-1}$). The quantum yields of **II** and **III** turned out to be independent of the light intensity.

2. Quencher Effect on Quantum Yield. Figure 2 shows plots for the quantum yields of reaction products φ_{II} and φ_{III} versus oxygen concentration for methanol and acetonitrile solutions. All the curves are satisfactory linear Stern–Volmer dependences. Oxygen can affect the quantum yields of the

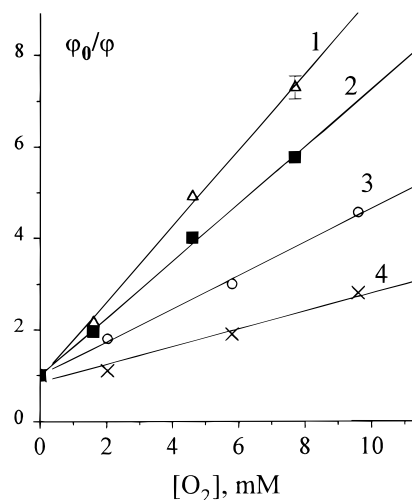


Figure 2. Stern–Volmer plots for product quantum yields vs oxygen concentration under low-intensity irradiation of a 1-naphthyl acetate solution (3×10^{-3} M). Quantum yield of **II** in acetonitrile (1) and in methanol (3), quantum yield of **III** in acetonitrile (2) and in methanol (4).

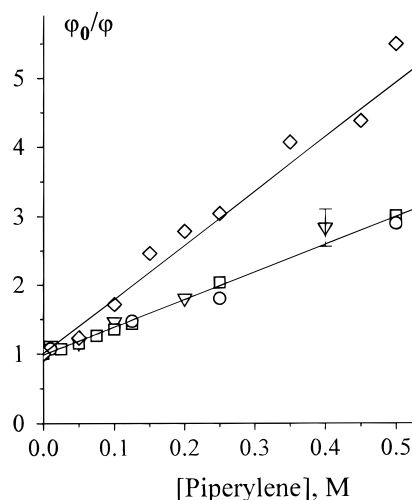


Figure 3. Stern–Volmer plots for the quantum yield of 2-acetyl-1-naphthol vs piperylene concentration under laser irradiation of 1-naphthyl acetate (3×10^{-3} M) in CH_3OH (triangles), CD_3OD (circles), and under Hg lamp irradiation in CH_3OH (squares), CH_3CN (diamonds).

products in different ways: via quenching triplet or singlet states or via reacting with the radicals arising in the photolysis. Indeed, in the presence of oxygen, the absorption spectrum of the product mixture changes: a protracted long-wave tail appears corresponding to oxygen-containing products.

Unlike oxygen, 1,3-pentadiene (piperylene) quenches mainly triplet states. However, the piperylene quenching of the excited singlet states of carbonyl compounds⁴⁰ and of the sodium salt of phenylsulfamic acid¹² has been reported. The addition of piperylene to the solution of **I** up to a concentration of 0.05 M does not affect significantly the quantum yield of the products, while the higher piperylene concentrations decrease the product yield (Figure 3). This can be described by Stern–Volmer plots with the slopes $7.8 \pm 0.8 \text{ M}^{-1}$ in acetonitrile and $4.0 \pm 0.3 \text{ M}^{-1}$ in methanol. Similar results have been obtained for methanol and acetonitrile under lamp and laser radiation. No changes in the ratio of product quantum yields ($\varphi_{\text{II}}:\varphi_{\text{III}}:\varphi_{\text{IV}}$) in the presence of piperylene have been revealed.

3. Sensitization of 1-Naphthyl Acetate Decomposition. The triplet state energy of **I** is estimated² as $E_{\text{T}} = 251.8 \text{ kJ/mol}$, which is lower than the corresponding value for naphthalene ($E_{\text{T}} = 254.7 \text{ kJ/mol}$).⁴¹ Phenanthrene ($E_{\text{T}} = 258.5 \text{ kJ/mol}$)

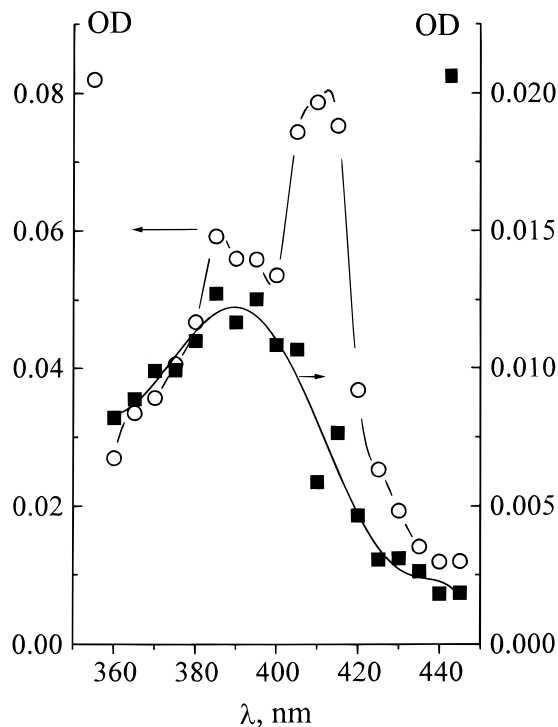


Figure 4. Transient absorption spectra observed 3 μ s (circles) and 22 μ s (squares) after laser pulse in a solution of 1×10^{-3} M 1-naphthyl acetate in acetonitrile.

mol),⁴¹ carbazole ($E_T = 294.1$ kJ/mol),⁴² and acetophenone ($E_T = 307.9$ kJ/mol),⁴¹ whose triplet states are known to be quenchable by naphthalene,⁴² were used as sensitizers. The sensitized photolysis was carried out under the radiation of the nitrogen laser at 337 nm where the absorption of **I** is negligibly small.

The quantum yield of **II** was very small for all the three sensitizers. The measurements for carbazole and acetophenone were complicated by photodecomposition of the compounds, followed by the formation of colored products. In sensitizing by phenanthrene, the quantum yield of **II** formed from the triplet state was estimated as $\varphi_T \leq 4 \times 10^{-3}$ (the yield of the sensitizer triplets was $\Phi_T = 0.8$).⁴¹

4. Laser Flash Photolysis of 1-Naphthyl Acetate (**I**).

Figure 4 shows the absorption spectra of intermediates, obtained during the photolysis of **I** in acetonitrile 3 μ s (circles) and 22 μ s (squares) after the laser flash. The first spectrum exhibits characteristic maxima at 385 and 410 nm. The main peculiarities of this spectrum coincide with those of the spectrum reported by Nagakura et al.⁵ and attributed to the 1-naphthoxyl radical. It is seen in Figure 4 that the absorption at 410 nm decays faster than that at 385 nm. Figure 4 shows that more than one intermediate absorbs in this region. A detailed analysis of the kinetic traces obtained at the absorption maximum at 410 nm allows us to conclude that at least two species contribute to the absorption at this wavelength. Immediately after the laser pulse the strong absorption signal (A) decays rapidly by the second-order law (Figure 5, upper trace), which testifies to the high initial concentration of the transient. In a long time scale the second, weak and slowly decaying, signal (B) can be distinguished; its decay also obeys the second-order law (Figure 6, upper trace).

The presence of piperylene even at small concentrations (about 10^{-4} M) strongly accelerates the decay of signal A. Figure 5 presents the kinetic traces obtained at 410 nm at different concentrations of piperylene. At the piperylene concentration 1×10^{-3} M the decay rate becomes independent of laser

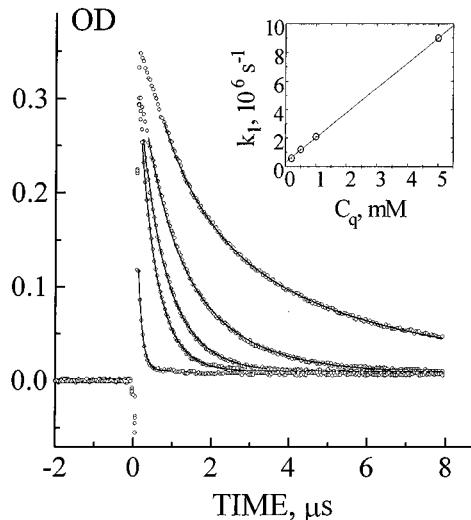


Figure 5. Transient absorption decay curves observed after excitation of a solution of 1×10^{-3} M 1-naphthyl acetate in acetonitrile in the presence of piperylene (signal A in text). The piperylene concentrations are 0 M (upper trace), 2×10^{-4} M, 5×10^{-4} M, 1×10^{-3} M, and 5×10^{-3} M (lowest trace). The monitoring wavelength was 410 nm. For calculated curves (solid lines) see text. Insert: the dependence of the first-order rate constant k_1 on piperylene concentration.

radiation power and can be described as a simple exponential curve. The initial intensity of the signal practically does not change until the quencher concentration becomes higher than 1 mM, whereas the rate of absorption decay increases significantly. Such behavior proves that the spectrum shown in Figure 4 by circles, as well as the spectrum reported by Nakagaki et al.,⁵ corresponds to the triplet state of **I** rather than to the 1-naphthoxyl radical. Proceeding from the shape of the absorption spectrum, Nakagaki et al.⁵ attributed the intermediate absorption to the 1-naphthoxyl radical. However, we believe that our spectrum (Figure 4, circles) as well as that reported by Nakagaki et al.⁵ are much closer to the T-T absorption spectrum of naphthalene.⁴³⁻⁴⁵ This is no wonder since the long-wave absorption spectrum of **I** is close to the absorption spectrum of naphthalene, with the bathochromic shift being no more than 150 cm^{-1} .

At the same time, the intensity and time behavior of the signal B change insignificantly in the presence of piperylene (Figure 6). We attributed the weak and slowly decaying signal, whose behavior only slightly depends on piperylene concentration, to the absorption of 1-naphthoxyl.⁴⁶ The top trace (Figure 6), obtained in the absence of quencher, exhibits the superposition of the remains of the triplet **I** signal and the radical absorption. The other traces correspond to 1-naphthoxyl radical: 10 μ s after the laser flash all triplet molecules should be quenched by piperylene. The decrease in the radical signal intensity is insignificant even at high piperylene concentrations.

Without triplet quencher, the triplet signal decays practically by the pure second-order law. It means that the triplet state of **I** is not very reactive, and the main channel of its decay is the triplet-triplet annihilation. The evolution of the optical density of the solution $D(t)$ is described by the equation

$$D(t) = \epsilon_T I T(t) = \epsilon_T I T_0 / (1 + k_{tt} T_0 t) \quad (1)$$

where ϵ_T is the triplet absorption coefficient, l is the optical path (1 cm), T_0 is the initial concentration of triplets, and k_{tt} is the rate constant of the T-T annihilation. In linear terms

$$1/D(t) = 1/D_0 + k_{tt} t / \epsilon_T l \quad (2)$$

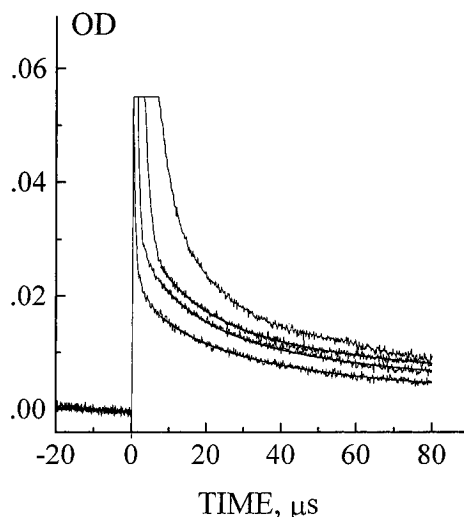


Figure 6. Transient absorption decay curves observed after excitation of a solution of 1×10^{-3} M 1-naphthyl acetate in acetonitrile in the presence of piperylene (signal B in text). The piperylene concentrations are 0 M (upper trace), 2×10^{-4} M, 5×10^{-4} M, and 5×10^{-3} M (lowest trace). The monitoring wavelength was 410 nm. Calculated curves are the second-order fit $[R] = [R]_0/(1 + k_t[R]_0t) + C$, $k_t = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; C is constant.

the slope of the straight line is determined by the ratio k_{tt}/ϵ_T . The experimentally determined value of k_{tt}/ϵ_T was independent of the light intensity varied within a factor of 5 and was equal to $(1.5 \pm 0.3) \times 10^6 \text{ cm/s}$ in acetonitrile and $(1.2 \pm 0.3) \times 10^6 \text{ cm/s}$ in methanol.

Unfortunately, our experiments do not allow us to determine the values of k_{tt} and ϵ_T separately. Nevertheless, we can compare the obtained value of k_{tt}/ϵ_T with those reported in the literature. It has been known that the T–T annihilation is a diffusion-controlled process;^{44,47,48} however, its rate can be essentially lower than that of the diffusion^{48,49} ($k_{tt} < 2k_{\text{dif}}$). The literature value⁴⁴ of k_{tt} for naphthalene in ethanol is $(1.8 \pm 0.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, whereas $2k_{\text{dif}}$ for ethanol is⁵⁰ $2.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Assuming that the latter relationship holds for **I** in acetonitrile, we may estimate the rate constant of the T–T annihilation in acetonitrile: $k_{tt} = (1.5\text{--}2.0) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, and, consequently, the triplet absorption coefficient $\epsilon_T = (1.2 \pm 0.6) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

Since the spectrum we detected is similar to the T–T absorption spectrum of naphthalene, it may be assumed that the values of the corresponding maximum absorption coefficients are close. For naphthalene, the maximum absorption coefficient at 414 nm, averaged over 16 literature values, is⁴⁵ $22\,500 \pm 5230 \text{ M}^{-1} \text{ cm}^{-1}$. For 1-methylnaphthalene the extinction coefficient averaged for six literature sources is somewhat lower than that for naphthalene ($\approx 15\,000 \text{ M}^{-1} \text{ cm}^{-1}$).⁴⁵ The value of ϵ_T for 1-naphthyl acetate seems to be about $10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Thus, the above estimation is in good agreement with the literature data.

The triplet-state quantum yield can be estimated by the comparison of the initial triplet concentration, extracted from the fit of eq 1, and the number of the light quanta absorbed by the initial compound during one laser pulse (for the last procedure see ref 27). For both the solvents, acetonitrile and methanol, the measurements were performed at three different laser pulse intensities (typical values 53, 21, and 10 mJ) and yielded similar results: $\varphi_T = 0.4 \pm 0.2$ and $\varphi_T = 0.35 \pm 0.15$ for acetonitrile and methanol, respectively. This can explain the relatively low yields of the products (Table 2): after the absorption of a light quantum, a significant part of the excited molecules undergo an intersystem crossing and transfer to a

low reactive triplet state. It is noteworthy that the reported² quantum yield of intersystem crossing for **I** (0.29) is consistent with our estimate.

The values of k_{tt} and ϵ_T obtained above were applied to the description of the curves recorded in the presence of piperylene (Figure 5) as a sum of the pseudo-first-order and second-order decays:

$$dT/dt = -k_1T - k_{tt}T^2 \quad (3)$$

$$k_1 = k_0 + k_qC_q \quad (4)$$

where k_0 is the rate constant of triplet state deactivation in the absence of piperylene and T–T annihilation, k_q is the quenching rate constant, and C_q is the quencher concentration. In this case, the evolution of the optical density of the T–T absorption $D(t)$ is determined by the equation

$$D(t) = \epsilon_T I T(t) = k_1 \epsilon_T I T_0 / [k_1 e^{k_1 t} + k_{tt} T_0 (e^{k_1 t} - 1)] \quad (5)$$

The initial triplet concentration T_0 and k_1 were the fitting parameters. The results for different piperylene concentrations, presented in the insert of Figure 5, give the values $k_q = (1.9 \pm 0.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_0 = (2.2 \pm 0.6) \times 10^5 \text{ s}^{-1}$ for acetonitrile.

An analysis of the absorption decay of the radicals not involved in the geminate recombination (Figure 6) has shown that the kinetics obey the second-order law. It is known that the reaction of radical termination is diffusion-controlled.⁵¹ We assumed that the rate constants of the bimolecular reactions of radicals in acetonitrile and methanol are typical for the termination rate constants⁵¹ $k_t = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Fitting the equation for the second-order decay to the experimental curves for different laser powers, we obtained the radical absorption coefficients $\epsilon_R = (4.7 \pm 1.0) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_R = (4.9 \pm 1.0) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ for acetonitrile and methanol, respectively. The values of initial radical concentrations extracted from this fitting allow one to estimate the quantum yields of the radicals not involved in the geminate recombination for the samples with high piperylene content as $\varphi_R = (2.6 \pm 0.8) \times 10^{-2}$ for acetonitrile and $\varphi_R = (6 \pm 2) \times 10^{-2}$ for methanol. The radical yield in methanol is higher than that in acetonitrile, which is consistent with our quantum yield values determined for these two solvents (Table 2).

5. CIDNP. Before proceeding to the consideration of the results obtained by the CIDNP method, we should note the following. An important feature of the chemical system under investigation is the formation of strongly absorbing products. Under intense laser radiation the optical density of the solution noticeably increases, which leads to a secondary photochemical reaction and complicates the quantitative interpretation of the experimental results. It has been established that irradiating the solution of each reaction product (**II**, **III**, and **IV**) does not lead to CIDNP. However, these compounds are photoactive and when irradiated can give rise to free radicals.⁴⁶ Thus, despite the insignificant conversion of an initial compound (below 5–7%), the experimental conditions at the beginning and at the end of irradiation could differ. Therefore we did not perform the quantitative analysis of the amplitude of CIDNP effects in the homogeneous processes.

The intensities of the CIDNP signals in the spectra obtained in the steady-state experiments depend on laser radiation energy and pulse repetition rate as well as on the time of irradiation and the nuclear relaxation times of protons. Therefore the results obtained by this method could be treated only qualitatively. The time-resolved CIDNP technique is free from these

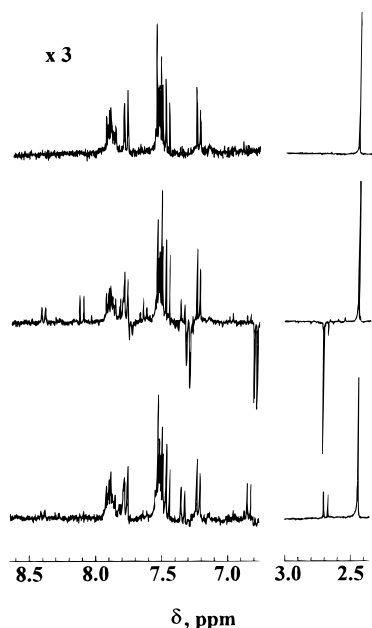


Figure 7. NMR ^1H spectra obtained before irradiation (upper spectrum), under steady-state irradiation (middle spectrum), and under steady-state irradiation in the presence of 0.2 M piperylene (lower spectrum) of 10^{-3} M 1-naphthyl acetate solution in methanol- d_4 .

disadvantages. However, under steady-state irradiation, the signal-to-noise ratio is much better than that in the time-resolved CIDNP experiments. It allows one to detect weak signals and reveal minor reaction pathways in the steady-state experiments.

The CIDNP spectra obtained under steady-state laser irradiation of **I** in methanol- d_4 are shown in Figure 7. A comparison between the CIDNP spectra and the NMR spectra of initial compound **I** and reaction products **II**–**IV** allows one to assign the polarized lines. The most intense emissive signals at 2.70 and 2.66 ppm belong to the methyl protons of **II** and **III**, correspondingly. In the aromatic region one can see three groups of emissive polarized signals. One of them is a doublet at 7.30 ppm, which corresponds to overlapping signals of the fourth protons of **II** and **IV**. The second group involves emissive lines at 6.8 ppm, which are attributed to the partially overlapping signals of the 2-protons of **III** (the doublet at 6.85 ppm with a splitting of 8.13 Hz) and the 2-protons of **IV** (the doublet at 6.79 ppm with a splitting of 7.15 Hz). The third group consists of weak emissive lines at 7.72–7.76 ppm, which are attributed to the 5-protons of **IV** and to the 3-protons of **II**, the positions of these lines coinciding. The emissive line at 2.08 ppm probably belongs to the ketene CH_2CO which is formed in the photolysis of **I**.⁵ The chemical shifts of the compounds under study in acetonitrile are slightly different from those given above; however, the corresponding CIDNP spectrum exhibits signals of the same products. Only in the steady-state CIDNP experiments did we succeed to detect the absorption signals of the minor product acetaldehyde (aldehyde proton, 9.89 ppm).

The addition of the triplet quencher piperylene (>10 mM) decreases the intensity of the CIDNP signals. The strong dependence of CIDNP on the presence of piperylene clearly indicates that the nuclear polarization appears in the radical pairs formed from triplet precursors. The same conclusion follows from the analysis of the polarization signs. The g factor of the acetyl radical (2.0005)⁵² is lower than that of naphthoxyl radical (2.00431),⁵³ and the hfi constant of acetyl protons is positive.⁵⁴ From time-resolved CIDNP experiments (see below) we know that the emission of the methyl protons of **II** and **III** is formed in cage. According to Kaptein's rules,⁵⁵ this leads to the

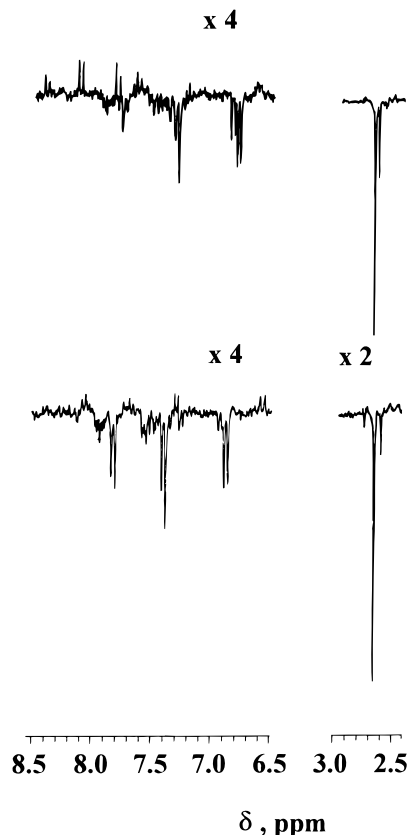


Figure 8. CIDNP spectra obtained 2 μs (upper spectrum) and 1000 μs (lower spectrum) after the laser flash in a solution of 10^{-3} M 1-naphthyl acetate in methanol- d_4 .

formation of a negative polarization of the in-cage products for the protons of the radicals with the lower g factor and a positive hfi constant in the case of triplet precursors. The emissive polarization of the acetyl groups of both **II** and **III** was detected. The hfi constants of the 2- and 4-protons of 1-naphthoxyl are negative (see Appendix) and correspond to the radical with the higher g factor. Thus, the emissive polarization of these protons in products **II**–**IV** is consistent with the assumption about the triplet precursor.

At a high piperylene concentration (0.2 M), the polarization sign changes from emission to absorption for the acetyl protons of both **II** and **III** (Figure 7), with the protons of **I** remaining unpolarized. At this concentration of piperylene, the signals in the aromatic region are too weak to be detected. The alteration of the CIDNP sign at high concentrations of piperylene indicates that **I** decomposes with the formation of radical pair through the singlet state as well.

Figure 8 shows the time-resolved CIDNP spectra obtained 2 μs (top spectrum) and 1000 μs (bottom spectrum) after the laser pulse. As in the steady-state experiments described above, the acetyl protons of **II** and **III** exhibit the most intense polarization. The kinetic analysis was performed only for these spectral lines. Figure 9 shows the kinetics of the net nuclear polarization of the protons of **II** (triangles) and **III** (squares), obtained during the photolysis of **I** in acetonitrile. Both the curves are characterized by an initial growth of the polarization. On passing the maximum I_m , the polarization decays in the microsecond time scale to the stationary value I_∞ . The ratio of I_m and I_∞ decreases with decreasing laser intensity, and the decaying section of the curve flattens. The CIDNP signals of **II**, obtained in acetonitrile at different laser intensities, show maxima 1.5 μs after the laser pulse; for **III** the kinetics is a maximum 5 μs after the flash. The kinetic curves for the nuclear

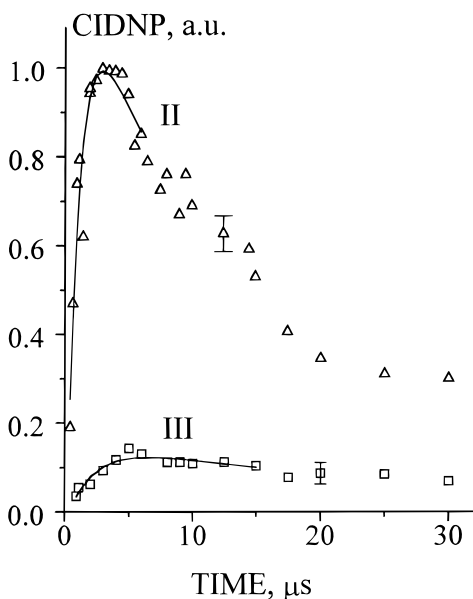


Figure 9. CIDNP kinetics (in arbitrary units) obtained during the photolysis of 1-naphthyl acetate in acetonitrile- d_3 for methyl protons of 2-acetyl-1-naphthol (triangles) and 4-acetyl-1-naphthol (squares). Solid lines is biexponential fit.

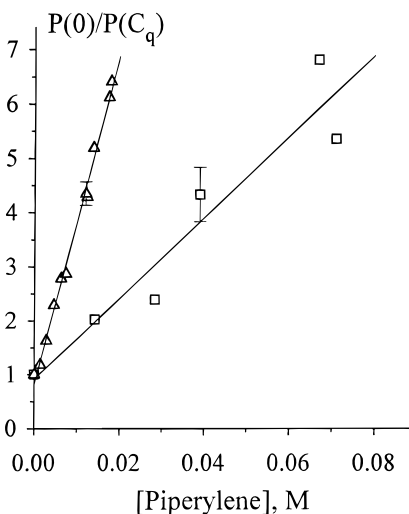


Figure 10. Stern–Volmer plots for the CIDNP intensity of methyl protons of 2-acetyl-1-naphthol vs piperylene concentration obtained during the photolysis of **I** in methanol- d_4 (triangles) and in acetonitrile- d_4 (squares).

polarization in methanol are similar to those corresponding to acetonitrile, but the polarization decay is less pronounced and the stationary value of CIDNP differs from its maximum value by no more than 25%. The solid line in Figure 9 is the result of biexponential fitting for the evolution of CIDNP signals. It is seen that the experimental and calculated curves are in good agreement, with the characteristic rise times being $\tau_2 = 0.9 \pm 0.1 \mu\text{s}$ and $\tau_3 = 2.2 \pm 0.2 \mu\text{s}$ for **II** and **III**, respectively.

In the presence of piperylene, the intensities of the CIDNP signals of acetyl protons of **II** and **III** decay drastically. Figure 10 shows the Stern–Volmer plots for CIDNP intensity at the kinetic curve maximum as a function of piperylene concentration for methanol and acetonitrile. The slopes of the curves are $k_Q = 302 \pm 10 \text{ M}^{-1}$ and $k_Q = 75 \pm 5 \text{ M}^{-1}$ for methanol and acetonitrile, respectively.

Consider now the formation of the triplet geminate CIDNP in the presence of a triplet quencher. By the time τ (1.5 μs) the geminate recombination is almost completed and the nuclear polarization arising in the homogeneous processes in the bulk

may be disregarded. The intensity of the geminate nuclear polarization is proportional to the number of the radical pairs (RP) resulting from the decomposition of the triplet states. The rate of RP formation is described by the equation

$$d[\text{RP}]/dt = k_r T(t) \quad (6)$$

Hence, the intensity P of geminate polarization is defined by the following integral:

$$P = \xi \int_0^\infty T(t) dt \quad (7)$$

where ξ is the polarization per one triplet-born radical pair (RP), and k_r is the rate constant of RP formation. In the general case, the time evolution of triplet states is described according to eq 5 with replacement of k_1 by k_r . Integration of (7) yields the expression for the CIDNP amplitude as a function of quencher concentration:

$$P(C_q) = \xi \frac{k_r}{k_{tt}} \ln \left(1 + \frac{k_{tt} T_0}{k_r + k_q C_q} \right) \quad (8)$$

All constants in eq 8 have been specified above. The dependence of the CIDNP signal intensity on quencher concentration is determined as follows:

$$P(0)/P(C_q) = \ln(1 + k_{tt} T_0/k_r) / \ln \left(1 + \frac{k_{tt} T_0}{k_r + k_q C_q} \right) \quad (9)$$

However, in our experiments (Figure 10), the dependence of CIDNP intensity on quencher concentration is linear. This corresponds to the condition $k_{tt} T_0/k_r \ll 1$. In this case the eq 9 takes the form of the Stern–Volmer equation:

$$P(0)/P(C_q) = 1 + k_q C_q/k_r \quad (10)$$

Using the quenching rate constants $k_q = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for acetonitrile and $k_q = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for methanol, determined in the flash photolysis experiments, we obtain from eq 10 the values $k_r = 3.3 \times 10^7 \text{ s}^{-1}$ for acetonitrile and $k_r = 5.2 \times 10^6 \text{ s}^{-1}$ for methanol.

Discussion

As one can see from Figures 3, 5, and 10, piperylene as a quencher affects the product quantum yields, the decay of triplets, and the CIDNP formation at different concentrations. Only very high piperylene concentrations ($\geq 0.1 \text{ M}$) affect the quantum yields of products; it means that the reaction proceeds from the extremely short-lived triplet state or, more likely, the product is formed directly from the first excited singlet state. In this case, the effect of piperylene can be regarded as the quenching of the excited singlet states that may occur at high quencher concentrations.^{12,40} Indeed, at sufficiently high piperylene concentrations, when most of the triplet molecules are quenched, we observe the alternation of the CIDNP sign as a manifestation of the singlet-born polarization. Earlier⁵ the conclusion that the products are formed in the singlet RP was drawn from the value of magnetic effect.

On the other hand, the strong dependence of CIDNP effects on the presence of piperylene in much lower concentrations ($\geq 0.002 \text{ M}$) and the signs of CIDNP signals clearly indicate that the nuclear polarization is created mainly in the radical pairs formed from triplet precursors. The change in the quantum yield of the reaction at such piperylene concentrations is negligibly small. Thus, we can conclude that both the singlet and triplet excited states of **I** participate in the formation of the initial

radical pairs. The triplet pathway of the reaction is of secondary importance. From the accuracy of the determination of quantum yields, one can estimate that the contribution of the triplet channel to the product formation is below 10%. However, it is this channel that is responsible for CIDNP formation. This is not surprising since usually the polarization formed through the singlet channel is weaker than that formed via the triplet precursor.

The absorption spectrum of the triplet state of **I** was obtained in the flash photolysis experiments. The validity of our attribution is strongly supported by the fact that in the presence of 10^{-4} – 10^{-3} M of piperylene the signal decay rate increases essentially, with the initial intensity of the signal being unchanged. At such concentrations, piperylene does not affect the quantum yield of the products. Our attribution of the intermediate absorption is consistent with the similarity of the spectrum of this intermediate to the T–T absorption spectrum of naphthalene. In the flash photolysis experiments, the main channel of the decay of the triplet states of **I** in the absence of quencher is the T–T annihilation. Very low concentrations of piperylene (about 10^{-4} M) appear to be sufficient to affect noticeably the decay rate of the triplet states. Thus, piperylene quenches the triplet state of **I** through T–T energy transfer, and the quenching process is expected to be diffusion-controlled.^{41,50} The rate constant of the piperylene quenching of the triplet state of **I**, measured in the flash photolysis experiments, k_q (1.9×10^9 M⁻¹ s⁻¹ in acetonitrile and 4×10^9 M⁻¹ s⁻¹ in methanol) is approximately an order of magnitude lower than the diffusion rate constant. However, this is no wonder since in this case the T₁ states of the donor (251.8 kJ/mol) and acceptor (238 and 245 kJ/mol for *cis*- and *trans*-piperylene, respectively)⁵⁶ are similar. Note that the value of k_q for 1-naphthol (T₁ energy 250 kJ/mol) is even smaller and equals 4.4×10^8 M⁻¹ s⁻¹ in an ether/hexane mixture.⁴⁶

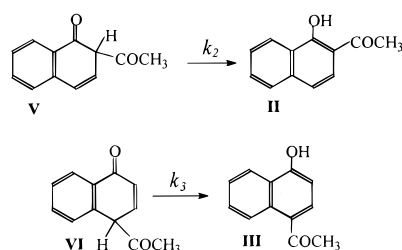
The lifetime of T₁ of 1-naphthyl acetate (in the absence of piperylene and T–T annihilation) is rather long: 4.5 ± 0.7 μs in acetonitrile solution (actually, this result, extracted from piperylene quenching of triplet states, could be affected by remains of oxygen in solution; the real lifetime is probably even longer). This value is inconsistent with the estimated lifetime of the triplet state responsible for the formation of RP and polarization as 30 ns for acetonitrile and 190 ns for methanol. It is seen that these lifetimes are 2 orders of magnitude shorter than those measured by flash photolysis. The qualitative difference is that in the flash photolysis experiments in the absence of quencher the T–T annihilation is the main decay channel of triplet molecules and the addition of 1 mM of piperylene decreases essentially the triplet lifetime (Figure 5). In the CIDNP experiments, where the exciting light intensity is the same, the T–T annihilation is no longer the main channel for the decay of the reactive triplet states and the addition of 1 mM of piperylene practically has no appreciable influence on CIDNP intensity.

It would be reasonable to assume that the different methods detect two different triplet states. A similar hypothesis about two reactive triplet states has been proposed for the photo-Fries rearrangement of phenyl sulfamates.¹² In the experiments on the flash photolysis of **I** we detect the spectrum of the lower (T₁) nonreactive $\pi\pi^*$ state, whose properties are similar to those of the triplet state of naphthalene. In the photo-Fries rearrangement, the reactive state is the upper short-lived triplet state (T₂) which decomposes to yield a radical pair of acyl and naphthoxyl radicals, wherein the CIDNP effects arise. The T₂ state is

probably the $n\pi^*$ triplet state. Estimations (see Appendix) show that in energy the $n\pi^*$ triplet state is to be between the singlet and triplet $\pi\pi^*$ states. Moreover, one may expect that T₂ can be quenched by piperylene with a rate constant k_q close to the diffusion one (about 1.5×10^{10} M⁻¹ s⁻¹ in acetonitrile and methanol).⁵⁰ Using this value of k_q , we estimate the lifetime of the reactive triplet state T₂ as 3 and 6 ns for acetonitrile and methanol, respectively. Further studies which are to validate or invalidate this hypothesis are in progress.

Let us discuss the nature of the maximum observed in the CIDNP kinetics (Figure 9). Usually the presence of a maximum in CIDNP kinetics is associated with the fact that the same products formed in the geminate cage and in the bulk have polarizations of opposite signs.⁵⁷ The nuclear polarizations of the geminate products and the radicals not involved in the in-cage recombination are the same in intensity and opposite in sign. If the nuclear paramagnetic relaxation time is long enough, the polarization carried out of the initial cage by radicals is transferred to the diamagnetic products in the course of the radical termination. This competition between geminate and homogeneous processes has been studied before.⁵⁷ According to theoretical calculations,⁵⁷ the maximum of a CIDNP kinetic curve should be positioned at $t_1 = (2k_t[R]_0)^{-1}$, and the intensity of the CIDNP signal at the maximum should not be more than 50% higher than the value of geminate polarization. In our case, the time behavior of the nuclear polarization differs from that predicted by Vollenweider and Fischer:⁵⁷ the intensity of CIDNP at zero point is negligibly small. Thus, we can conclude that the formation of the geminate polarization is protracted in time. This protraction can arise from the following. First, the absence of the signal at the initial time can be due to the nonzero lifetime of the reactive triplet state. According to the above estimations, the lifetime of the reactive triplet state is several nanoseconds. Such a short lifetime cannot be responsible for the position of the maximum of CIDNP kinetics.

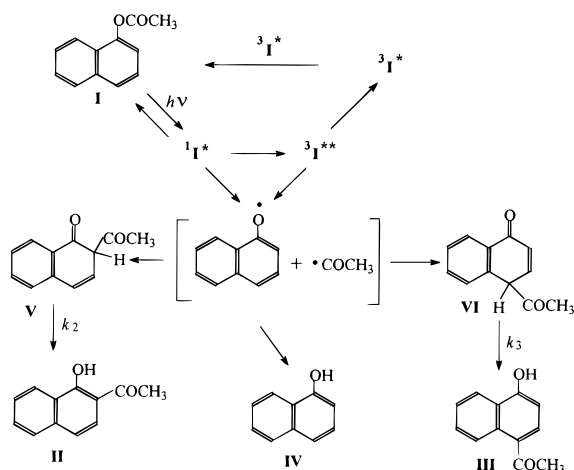
The kinetics of the increasing geminate CIDNP can be accounted for by another hypothesis. We assume that the detected kinetics depends on the process of the formation of compounds **II** and **III** from intermediate unstable adducts **V** and **VI**, respectively. The estimation of the rate constants of



these processes as the rate of signal increase in flash-CIDNP experiments (Figure 9) gives the values $k_2 = (1.1 \pm 0.1) \times 10^6$ s⁻¹ and $k_3 = (4.5 \pm 0.5) \times 10^5$ s⁻¹ for acetonitrile. It has been known²⁴ that the lifetimes of cyclohexadienones, which are intermediates of the photo-Fries rearrangements of phenyl acetate, increase essentially in polar and particularly in protic solvents. In alcohols (EtOH, MeOH), the rate constants for 1,3- and 1,5-hydrogen shifts reach values of about 10^5 s⁻¹, which are close to the results of our measurements.

The results obtained allow us to propose the mechanism for the photo-Fries rearrangement of 1-naphthyl acetate (Scheme 2). The 1-naphthyl acetate (**I**) molecule that has absorbed a photon passes into the excited singlet state ¹I*. After that the major portion of the excited singlet states (according to Table 2, from 0.17 ± 0.02 in acetonitrile to 0.42 ± 0.04 in methanol)

SCHEME 2



decays to the radical pairs of acetyl and naphthoxyl radicals. The remaining excited molecules undergo the intersystem crossing and transfer into the triplet states T_2 ($^3I^{**}$) and T_1 ($^3I^*$). Most of the singlet-born radicals recombine in the initial cage to form **V** and **VI**, which then are rearranged into **II** and **III**. The rest radicals escape and decay in bulk reactions.

The arising triplets $^3I^*$ (T_1) are low-reactive. The quantum yields of the triplet states arising under laser flash radiation are 0.4 ± 0.2 and 0.35 ± 0.17 for acetonitrile and methanol, respectively. The T–T annihilation is the main channel of their decay. The fact that the yield of the products under laser irradiation coincides with that under lamp irradiation as well as the extremely low quantum yield of the products in the sensitized photolysis indicates that the triplet states $^3I^*$ mainly decay without reaction even at the lower light intensities. The results obtained by the CIDNP method suggest that at least some $^3I^{**}$ (T_2) react to form radical pairs. The CIDNP created in such pairs is higher than the nuclear polarization formed in the singlet-born pairs.

It has been concluded that the total contribution of the triplet channel to photo-Fries rearrangement is small ($<10\%$). This can be accounted for by the fact that the higher reactive triplet state $^3I^{**}$ (T_2) converts fast into the nonreactive triplet state $^3I^*$ (T_1) in the internal conversion, and this channel competes with the $^3I^{**}$ decay to radicals. The nonreactive nature of the triplet state T_1 is unlikely to be determined by its orbital nature. According to the recent theoretical work of Grimme,²² the primary process in the photo-Fries rearrangement is treated as the $\pi\sigma^*$ -induced photodissociation. The C–O bond fission can start from both the $n\pi^*$ and $\pi\pi^*$ states. The photodissociation process is activated, with the barriers formed due to the crossing of $n\pi^*$ or $\pi\pi^*$ with repulsive $\pi\sigma^*$ potential curves.²² It has been estimated (see Appendix) that the C–O bond dissociation occurring through the excited singlet and second triplet states is an essentially exothermic process. In the lower $\pi\pi^*$ triplet state ($^3I^*$) the enthalpy of the reaction is small. Therefore, in this case, the activation barrier of the dissociation should be very high and, hence, the dissociation should be low-efficient.

The essentially higher activation barrier of the photo-Fries rearrangement of 1-naphthyl acetate with respect to the corresponding value for phenyl acetate³ appears to be associated with the lower energy of the excited singlet state of 1-naphthyl acetate (383.4 kJ/mol, see Appendix) as compared to the corresponding energy value for phenyl acetate (421.5 kJ/mol).²²

Conclusions

In this work, we have employed a number of experimental methods for a detailed investigation of the phototransformation

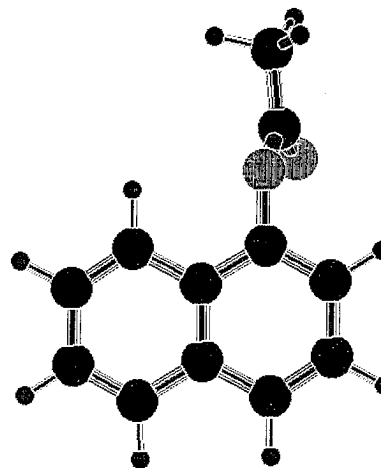


Figure 11. Computer-generated drawing of the 1-naphthyl acetate structure.

of 1-naphthyl acetate, which is a typical photo-Fries rearrangement reaction. The analysis of the effect of piperylene on the quantum yield of reaction products and on the signs of polarization observed in CIDNP spectra has validated the assumption that the decomposition of 1-naphthyl acetate to acetyl and naphthoxyl radicals through the singlet state is the main channel of the reaction (not less than 90%). The analysis of the CIDNP spectra shows that recombining radical pairs do not form initial 1-naphthyl acetate.

Although the reaction goes mainly through the singlet channel, the major contribution to CIDNP is made by the radical pairs resulting from the decomposition of the upper triplet states of 1-naphthyl acetate. Analyzing the kinetics of the polarization of photo-Fries rearrangement products (2-acetyl- and 4-acetyl-1-naphthol) we have established that the products are formed in the geminate cage as well as in the bulk. The unusual CIDNP kinetics, with the polarization absent at short times, indicates that the formation of geminate polarization is protracted in time. The most likely limiting stage of CIDNP formation in the products is the isomerization of intermediates. The absence of polarization of the 1-naphthyl acetate protons is indicative of the fact that the recombination of the naphthoxyl and acyl radicals to the initial compound is insignificant and, hence, is not responsible for the essential difference of the quantum yield of the photo-Fries rearrangement from unity.

In the flash photolysis experiments we have detected the absorption spectra of 1-naphthyl acetate triplet and naphthoxyl radicals; their absorption coefficients have been estimated. It has been established that the quantum yield of the triplet state of 1-naphthyl acetate is sufficiently high and the main channel of triplet decay is the triplet–triplet annihilation. This is consistent with the fact that the quantum yield of the photo-Fries rearrangement of 1-naphthyl acetate is much less than unity (0.17 in acetonitrile and 0.42 in methanol).

Proceeding from the different effects of piperylene on the decay kinetics of T–T absorption and on the yield of CIDNP via the triplet channel, we propose that the upper triplet state participates in the photo-Fries rearrangement of 1-naphthyl acetate. Further investigations are carried out in order to validate or invalidate this assumption.

Appendix. Quantum Chemical Calculations

Figure 11 shows the results of the AM1 calculation of 1-naphthyl acetate geometry. It can be seen that the plane of the acyl group (COC atoms) is practically perpendicular ($\theta = 84^\circ$) to the plane of naphthalene rings. The rotation barrier of

TABLE 3: Calculated and Experimental Values of Maxima in the Absorption Spectra of 1-Naphthyl Acetate (λ_{\max}), Experimental Values of the Absorption Coefficients at the Maxima (ϵ), and Calculated Values of Oscillator Strengths (f)

expt λ_{\max} (log ϵ)	calc λ_{\max} (f)
313 (2.60)	304 (0.011)
280 (3.80)	274 (0.100)

TABLE 4: INDO (UHF) Calculations and Experimental Values for ^1H hfi Constants (a , mT) in 1-Naphthoxyl Radical

	H2	H3	H4	H5	H6	H7	H8
calc	-0.89	0.53	-0.95	-0.38	0.28	-0.35	0.32
exp ⁵⁹ (abs val)	0.825	0.175	1.075	0.25	0.065	0.25	<0.04

TABLE 5: INDO (UHF) Calculation for Spin Density Distribution in 1-Naphthoxyl

C2	C3	C4	C5	C6	C7	C8	O
0.26	-0.07	0.28	-0.05	0.07	-0.04	0.07	0.53

the acyl group in 1-naphthyl acetate is 9.6 kJ/mol. The MNDO and PM3 calculations also give large angles of rotation of the acyl group with respect to the ring plane (80° and 70°, respectively). The AM1 calculation of the heat of C—O bond dissociation gives 227 kJ/mol (compare with 186 kJ/mol for PM3 and 212 kJ/mol for MNDO).

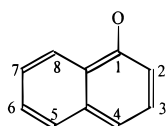
On the basis of the similarity of the 1-naphthyl acetate and naphthalene spectra and the known positions of the lower triplet and singlet states of naphthalene,⁴¹ one can estimate the positions of the lower singlet and triplet $\pi\pi^*$ states of 1-naphthyl acetate, which are 383 and 252 kJ/mol, respectively. From these data and the heat of the bond dissociation we obtain the heat of the dissociation $\Delta H^S = -156$ kJ/mol in the singlet state and $\Delta H^T = -24.7$ kJ/mol in the lowest triplet state.

It follows from our experimental data that the lowest triplet state is nonreactive in the photo-Fries rearrangement. The small contribution of the triplet channel to the photorearrangement could be explained by the participation of the $n\pi^*$ triplet state. The results of the CNDO/S calculation⁵⁸ of the absorption spectrum of 1-naphthyl acetate are listed in Table 3.

The calculated spectrum fits well the experimental one ($\pi\pi^*$ states, Table 3). For the $n\pi^*$ state the calculation gives $\lambda_{\max} = 299$ nm. Hence, the $\pi\pi^*$ singlet and triplet states are the lower excited states of 1-naphthyl acetate. Assuming that the singlet–triplet splitting for the $n\pi^*$ states^{41,42} is $(2-4) \times 10^3$ cm⁻¹, one can estimate the position of the $^3n\pi^*$ state, which is 327–352 kJ/mol. For the heat of the dissociation in this triplet state we have $\Delta H^T = -(100-126)$ kJ/mol.

The reaction of radical recombination, yielding intermediate adducts, is naturally an exothermic one. If adduct **V** is formed, the AM1-calculated enthalpy of the reaction is -199 kJ/mol, while the enthalpy of the formation of adduct **VI** is -191 kJ/mol. The reactions of adducts **V** and **IV** to the final products (**II** and **III**) are also exothermic ($\Delta H = -53$ and -41 kJ/mol, respectively). However, the isomerization rate constants increase essentially (by 5–6 orders of magnitude in proton-donor solutions, e.g., in alcohols), which indicates that solvent protons are involved in the reaction.²⁴

The spin density distributions and ^1H hfi constants for the 1-naphthoxyl radical have been calculated (Tables 4 and 5).



It is seen from Table 4 that the calculated values of negative ^1H hfi constants are in good agreement with the corresponding experimental values, with the positive values of the hfi constants being overestimated. Both theoretical and experimental data suggest that the hfi constant with hydrogen in position 4 is higher than that in position 2. This is consistent with the data of Table 5, which show that the spin density on carbon in position 4 is higher than that in position 2.

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