

## Investigation of the photo-Fries rearrangement reactions of 1- and 2-naphthyl acetates

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### Abstract

The investigation of the photo-Fries reaction of 1- and 2-naphthyl acetates (1- and 2-NAs) was performed using stationary photolysis, laser flash photolysis and steady state and time-resolved chemically induced dynamic nuclear polarization (CIDNP). The transient absorption spectra of the 1- and 2-naphthoxyl radicals and the 1-NA and 2-NA triplet states were detected, and the quantum yields and absorption coefficients were obtained. The influence of a triplet quencher on the naphthoxyl radical quantum yield was studied, and the singlet nature of the primary radical pair was confirmed for both initial compounds. On laser flash photolysis of 1-NA, the formation of the ortho product was directly detected, and the rate constant of the [1,3] hydrogen shift reaction was established. The signs of the CIDNP signals during the photolysis of 2-NA point to a singlet precursor of the radical pair giving rise to the rearrangement products, and to a triplet precursor for the disproportionation products of the parent radical pair. A comparison of the slopes of the Stern–Volmer plots for the rearrangement product quantum yield, for triplet CIDNP, and for the optically detected 2-NA triplet state confirms the previously reported assumption about the main role of the excited singlet state and the involvement of two different triplet states in the reaction. A general kinetic scheme for 1- and 2-NA photolysis is proposed. © 1997 Elsevier Science S.A.

**Keywords:** Naphthyl acetates; Photo-Fries rearrangement

### 1. Introduction

The photolysis of 1- and 2-naphthyl acetates (1- and 2-NAs) is a typical photo-Fries rearrangement reaction [1]. From the chemical point of view, the unifying feature of all photo-Fries reactions is the 1,3 migration (or 1,5 and 1,7 migrations) of an R–CO group from the initial aryloxy position. These reactions are of obvious academic interest. Moreover, they appear to play a significant role in the degradation of polycarbonates, polyesters and polyamides [2]. Since they were first discovered [3], the photo-Fries reactions of aryl esters [1–7] and of various aromatic compounds [8–13] have been investigated extensively. The radical mechanism of these reactions is well established [14,15], and is believed to involve the homolytic cleavage of the carbon–heteroatom bond [16]. Radical pair formation is followed by recombination, disproportionation [17] and hydrogen abstraction processes [1]. Chemically induced dynamic nuclear polarization (CIDNP) spectra [18], the absence of triplet sensitization [1] and the sign of the external magnetic field effect

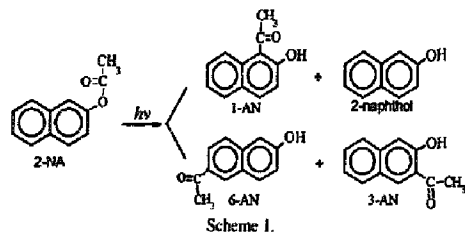
[6] indicate that the reaction occurs mainly through the excited singlet state.

Recently, we performed a detailed study of the phototransformation of 1-NA in different solvents [7]. It was shown that the main reaction pathway involves the formation of singlet radical pairs, whereas the main contribution to CIDNP effects is made by triplet radical pairs. In laser flash photolysis experiments, the kinetics of 1-naphthoxyl radicals have been obtained, as well as the transient absorption of a non-reactive long-lived triplet state. The involvement of two different triplet states of the initial molecule has been proposed. A similar hypothesis was assumed previously for phenylsulfonates [13] and aryl cinnamates [19].

This work has three main goals:

1. to test our newly constructed laser flash photolysis arrangement;
2. to obtain additional spectroscopic and kinetic information on 1-NA photolysis which was missed or misinterpreted in our previous paper [7];
3. to carry out analogous investigations of 2-NA photolysis and to compare the mechanisms of photolysis of these two similar compounds.

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As in Ref. [7], we used the complementary methods of stationary and laser flash photolysis and steady state and time-resolved CIDNP.

According to Refs. [20–22], the irradiation of 2-NA gives rise to products typical of rearrangement reactions: 1-acetyl-2-naphthol (1-AN), 3-acetyl-2-naphthol (3-AN), 6-acetyl-2-naphthol (6-AN) and 2-naphthol (Scheme 1). The distribution of products varies in different solvents, but the main products are 1-AN and 2-naphthol; moreover, the sum of their quantum yields remains constant (70%–80% of the total yield) over a wide range of temperatures and solvents [22]. So far, no evidence for the involvement of the triplet excited state in the reaction has been reported.

## 2. Experimental details

### 2.1. Materials

1- and 2-NAs from "Chemapole" were additionally purified by recrystallization from a water–ethanol mixture (1 : 9). The main product of 2-NA photolysis, 1-AN, was synthesized as described in Ref. [23]. Methanol and acetonitrile were distilled over Na. Deuterated solvents,  $CD_3CN$  and  $CD_3OD$  (99% enriched), from "Isotope" were used as received. 1,3-Pentadiene (piperylene) was distilled and contained both *cis* and *trans* isomers.

### 2.2. Stationary photolysis

Argon was bubbled through solutions of 2-NA in a quartz cell and the solutions were irradiated with an XeCl excimer laser (308 nm; 30 mJ per pulse) with continuous mixing. Piperylene was added when needed after bubbling to maintain its concentration. Radiation-induced changes in the absorption spectra were detected using a UV-VIS-202 (Shimadzu) spectrophotometer. The degree of conversion was kept below 5% in order to avoid secondary photochemistry. The quantum yields of the products were determined both spectroscopically and by chromatographic analysis of the reaction mixture on a high performance liquid chromatography (HPLC) "Mili-chrom-4" apparatus with UV detection, using the absorption coefficients of the products reported in Ref. [21].

### 2.3. Laser flash photolysis

Our newly constructed laser flash photolysis apparatus is similar to that recently built at Zurich University [24]. The

radiation from a home-built XeCl excimer laser (308 nm; pulse energy up to 150 mJ; pulse duration, 15 ns) was passed through a shutter and a home-built joulemeter, and concentrated by spherical lenses onto a quartz cell (inside dimensions, 2 mm  $\times$  10 mm  $\times$  100 mm; area of the laser beam 4 mm  $\times$  8 mm at the cell front). The sample solution flowed through the cell at a rate of 3 cm<sup>3</sup> min<sup>-1</sup>, replacing the solution in the photolysis region after each laser pulse.

The monitoring system consisted of a 150 W short-arc Xe lamp (DKsSh-150) equipped with a home-built pulser (pulse duration, 2 ms; rectangular monitoring beam with dimensions inside the cell of 2 mm  $\times$  3 mm), two synchronously operating home-built monochromators (200–680 nm; 1200 grooves mm<sup>-1</sup>), a set of spherical lenses, a shutter and a Hamamatsu R955 photomultiplier (five dynodes; total voltage up to 1000 V). The monitoring light beam was perpendicular to the exciting laser beam. The photomultiplier signal was measured over a 50  $\Omega$  resistor by a digital oscilloscope (LeCroy 9310A; 11 bit-ADC; time resolution, 10 ns). Triggering of the oscilloscope was synchronized with the laser pulse.

Our apparatus was completely computer controlled via an MP4888CT IEEE488 interface. To obtain one kinetic curve, 10–50 traces were averaged and transferred to a PC. The corrections for the lamp profile and fluorescence were made by subtracting the signals obtained for the different configurations of the shutters.

Before the measurements, all solutions were purged with argon for at least 30 min to remove oxygen. The optical density of the solutions at 308 nm was kept below 0.2 at 2 mm. The initial concentrations of the excited species were determined as described previously [24].

### 2.4. CIDNP

All of the <sup>1</sup>H nuclear magnetic resonance (NMR) and CIDNP spectra were taken on a Bruker MSL-300 FT-NMR spectrometer using the optical arrangement described previously [7]. In the steady state CIDNP experiments, samples were irradiated for 1 s by ten laser pulses. CIDNP effects were determined as the difference between the spectra obtained during and after irradiation. Time-resolved CIDNP spectra were obtained according to the conventional technique [7].

The optical density of the solutions at 308 nm was about 0.4 in 5 mm sample tubes. All samples were purged by argon prior to use; the content of piperylene was controlled by NMR spectroscopy.

## 3. Results and discussion

### 3.1. Stationary photolysis

From the stationary photolysis of 2-NA, the quantum yield of 1-AN was established spectrophotometrically using the

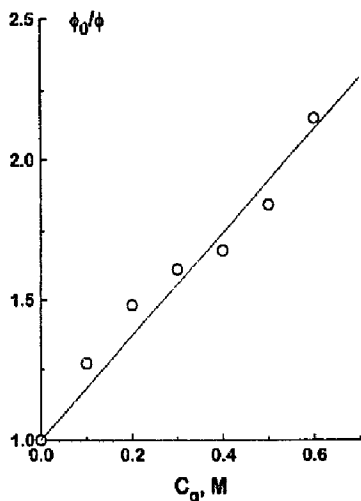


Fig. 1. Stern-Volmer plot of the 1-AN quantum yield vs. piperlyene concentration for the photolysis of 2 mM 2-NA in acetonitrile.

absorption coefficient at 357 nm ( $4390 \text{ M}^{-1} \text{ cm}^{-1}$ ) [21]. At concentrations of 2-NA within  $10^{-3}$ – $10^{-2}$  M, the quantum yield of 1-AN is  $3\% \pm 0.6\%$  in acetonitrile and  $2.5\% \pm 0.6\%$  in methanol. The quantum yield of this product, established by the HPLC technique, is the same, and for 2-naphthol is about 2% in acetonitrile. We registered only trace amounts of the products 3-AN and 6-AN, which could not be measured in our experiments. Thus the main products of the photo-Fries reaction of 2-NA are 1-AN and 2-naphthol, which is in good agreement with previous reports [20–22].

The effect of quencher on the quantum yield was studied by the addition of piperlyene to the initial solution. The slope of the corresponding Stern-Volmer plot (Fig. 1) for the quantum yield of 1-AN is  $1.9 \pm 0.2 \text{ M}^{-1}$  in acetonitrile. The other product, 2-naphthol, exhibits the same quantum yield dependence, detected by HPLC measurements. Such a small slope of the Stern-Volmer dependence indicates an extremely short-lived excited state as the precursor of the radical pair, probably the first excited singlet state.

### 3.2. Laser flash photolysis

Figs. 2 and 3 (circles) show the transient absorption spectra obtained 0.5  $\mu\text{s}$  after the photolysis of  $10^{-3}$  M solutions of 1-NA and 2-NA respectively. The temporal changes in the spectra are similar to those reported in Ref. [7] for 1-NA photolysis: the long-wavelength shoulder decays more rapidly than the short-wavelength shoulder. This suggests the involvement of at least two absorbing intermediates. Further consideration shows that these spectra mainly correspond to the triplet-triplet (T-T) absorption of 1-NA and 2-NA. The addition of the triplet quencher piperlyene strongly accelerates the decay of the signal monitored at the absorption maximum (417 nm for 1-NA and 410 nm for 2-NA), while the initial absorption remains unchanged.

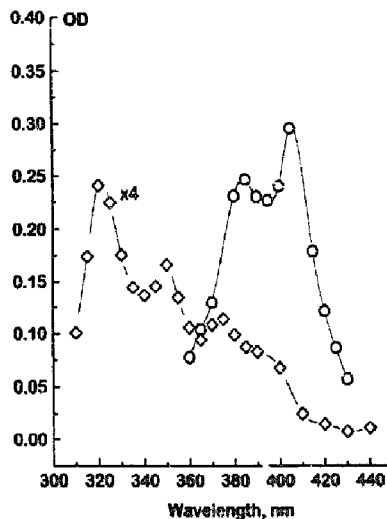


Fig. 2. Transient absorption spectra of triplet 1-NA (circles, 0.5  $\mu\text{s}$  after the laser pulse) and the 1-naphthoxyl radical (diamonds, 5  $\mu\text{s}$  after the laser pulse, in the presence of 3 mM piperlyene) obtained during the photolysis of 1 mM 1-NA in acetonitrile.

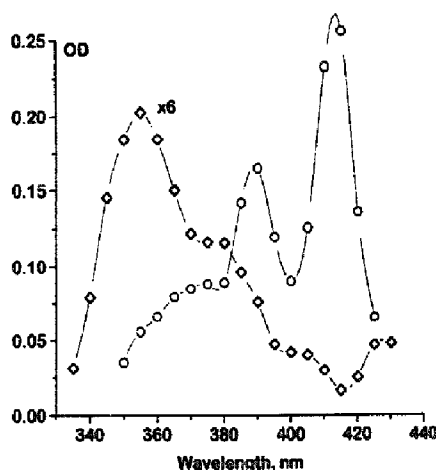


Fig. 3. Transient absorption spectra of triplet 2-NA (circles, 0.5  $\mu\text{s}$  after the laser pulse) and the 2-naphthoxyl radical (diamonds, 5  $\mu\text{s}$  after the laser pulse, in the presence of 3 mM piperlyene) obtained during the photolysis of 1 mM 2-NA in acetonitrile.

Experiments carried out at different laser energies show that the decay of the 2-NA triplet, monitored at 410 nm in the absence of the quencher, obeys a second-order law. Presuming that the triplet-triplet annihilation takes place with a rate close to the diffusional rate  $k_{\text{T-T}} = 1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  [7], the fitting procedure gives a triplet absorption coefficient  $\epsilon_{\text{T}}$  of  $18300 \pm 5500 \text{ M}^{-1} \text{ cm}^{-1}$  and a triplet quantum yield  $\phi_{\text{T}}$  of  $17\% \pm 2\%$ . Earlier [7], the triplet quantum yield of 1-NA photolysis was found to be  $\phi_{\text{T}} = 40\%$ .

In the presence of piperlyene, the triplet decay can be described by the following equation

$$\begin{aligned}
 -dT/dt &= (k_0 + k_q \times C_q) \times T + k_{TT} \times T^2 \\
 &= k_1 \times T + k_{TT} \times T^2
 \end{aligned}
 \quad (1)$$

where  $T$  is the concentration of triplets,  $k_1$  is the effective rate constant of the pseudo-first-order decay,  $k_0$  is the rate constant of the first-order triplet state decay in the absence of quencher,  $k_q$  is the quenching rate constant and  $C_q$  is the quencher concentration. The solution of Eq. (1) gives the following expression for the transient optical density of the solution

$$\begin{aligned}
 D(t) &= \epsilon_T \times I \times T \\
 &= k_1 \times \epsilon_T \times I \times T_0 / [k_1 \times e^{k_1 t} + k_{TT} \times T_0 \times (e^{k_1 t} - 1)]
 \end{aligned}
 \quad (2)$$

$k_1$  and  $T_0$  were fitting parameters in our calculations. The extracted values of  $k_1$  exhibit a linear dependence on the quencher concentration (Fig. 4). This plot gives a value of  $k_q$  of  $(2.1 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and of  $k_0$  of  $(3.6 \pm 0.3) \times 10^5 \text{ s}^{-1}$  for 2-NA photolysis in acetonitrile. We should note that the value of  $k_0$  is probably determined by the remaining oxygen or solvent impurities in the solution. This is also valid for  $k_0 = (2.2 \pm 0.6) \times 10^5 \text{ s}^{-1}$  reported for 1-NA photolysis in acetonitrile [7].

The diamonds in Figs. 2 and 3 show the transient absorption spectra obtained during the photolysis of 1-NA and 2-NA respectively in the presence of 3 mM piperylene 5  $\mu\text{s}$  after the laser flash, when all triplets are already quenched. These spectra coincide well with the spectra of the 1- and 2-naphthoxyl radicals obtained during the photolysis of 1- and 2-naphthols under the same conditions. The kinetic behaviour of the 1-naphthoxyl radical formed during the photolysis of 1-NA has been described previously [7]. The absorption of the 2-naphthoxyl radicals also decays by a second-order law, and the initial absorption depends only slightly on the presence of piperylene in the solution. Indeed, the Stern–Volmer

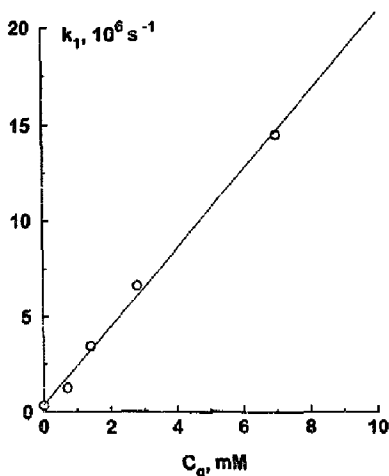


Fig. 4. Dependence of the effective first-order rate constant of 2-NA triplet state decay on the piperylene concentration.

dependence of the initial radical absorption on the piperylene concentration is similar to that of the product quantum yield. This finding confirms that both the radicals and the products are formed mainly via the singlet channel.

Fitting the radical decay to second-order reaction kinetics with the typical radical termination rate constant  $k_t = 8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for acetonitrile gives a radical absorption coefficient  $\epsilon_R$  of  $5900 \pm 2200 \text{ M}^{-1} \text{ cm}^{-1}$  at 380 nm and a radical quantum yield  $\phi_R$  of  $1.2\% \pm 0.6\%$ .

At the maximum of the absorption band (360 nm) of the main product of 1-NA photolysis, 1-AN, we directly detected the formation of this product. The intensity of the signal at 360 nm increases monoexponentially (Fig. 5), and the rate constant of this process is independent of the initial radical concentration and the presence of piperylene in the solution. Thus this process can be attributed to the isomerization reaction  $A \rightarrow B$ , where A is the intermediate product (adduct) formed by the recombination of 1-naphthoxyl and acyl radicals (to the ortho site of the 1-naphthoxyl ring) and B is the final ortho product (1-AN) (Scheme 2).

This signal was treated by fitting the parameters in Eq. (3)

$$\begin{aligned}
 D(t) &= A_0 \times e^{-k_t t} + B_0 \times (1 - e^{-k_t t}) \\
 &= (A_0 - B_0) \times e^{-k_t t} + B_0
 \end{aligned}
 \quad (3)$$

which reflects the absorption of both the intermediate product A and the final product B. The rate constant  $k_t$  was found to be  $(1.7 \pm 0.3) \times 10^4 \text{ s}^{-1}$ , which implies a lifetime of A of about 60  $\mu\text{s}$ .

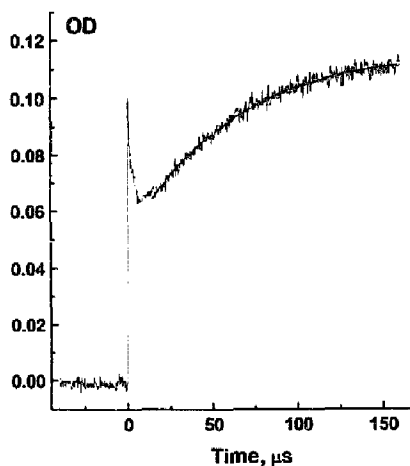
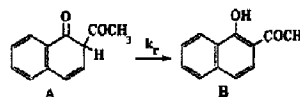


Fig. 5. Kinetics of 1-AN formation monitored at 360 nm during the photolysis of 1 mM 1-NA in acetonitrile (for calculated curve, see text).



Scheme 2. The [1,3] hydrogen shift reaction in the intermediate molecule 1-oxo-2-aceto-1,2-dihydronaphthalene.

The reaction of isomerization is the slowest elementary stage and, therefore, determines the overall rate of the photo-Fries reaction. Our previously reported value of  $k_r = (1.1 \pm 0.1) \times 10^6 \text{ s}^{-1}$  [7] was based on an incorrect interpretation of CIDNP kinetics and is not tenable. For the similar reaction of phenyl acetate photolysis, the lifetimes of the ortho adduct of phenyl acetate have been reported to be about 20 ms in acetonitrile and about 2  $\mu\text{s}$  in methanol [25].

Our attempts to detect the same reaction of isomerization in the photolysis of 2-NA failed, probably because the difference in absorption between the intermediate and final products was too small even at the maximum of the absorption band of the latter.

### 3.3. CIDNP results

In Fig. 6, the steady state CIDNP spectrum of 2-NA in  $\text{CD}_3\text{OD}$  is presented; the spectrum in  $\text{CD}_3\text{CN}$  differs from the latter by the lower intensity of the signal at 2.14 ppm. These spectra exhibit intense emissive CIDNP at 7.08 ppm and 2.14 ppm and absorptive CIDNP at 2.70 ppm. The emissive line at 2.14 ppm probably belongs to the ketene  $\text{CH}_2\text{CO}$  [26], formed by disproportionation [7,17]. The following observations confirm the assignment of this line to the ketene:

1. the chemical shift of this line corresponds to none of the other possible products of the acyl radical reactions (i.e. diacetyl, acetaldehyde, acetic acid);
2. in the NMR spectrum of the reaction products, obtained after prolonged irradiation of 3 mM 2-NA in  $\text{CD}_3\text{OD}$ , no signal at 2.14 ppm is obtained; this means that the CIDNP

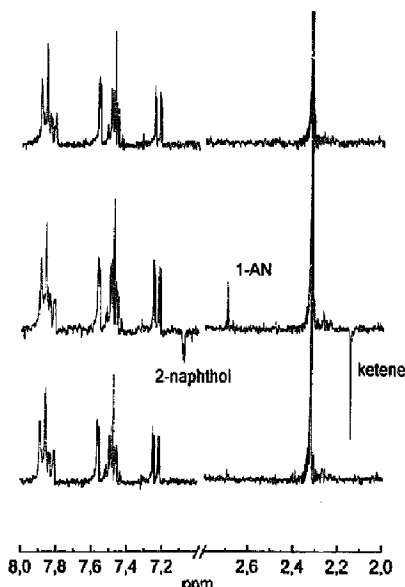


Fig. 6. NMR spectra of 2-NA in  $\text{CD}_3\text{OD}$  obtained before irradiation (top spectrum), on irradiation by laser pulses for 1 s with a repetition rate of 10 Hz (middle spectrum) and after irradiation (bottom spectrum).

signal at 2.14 ppm can be attributed to an unstable product which disappears on a timescale of seconds or minutes;

3. the signals of methyl acetate (2.01 ppm) and acetic acid (1.98 ppm), which can appear in the reactions of ketene with methanol and residual water respectively, are observed in the NMR spectrum of the reaction products.

The other emissive signal at 7.08 ppm is attributed to the protons of 2-naphthol. The absorptive line at 2.70 ppm can be attributed to the methyl protons of 1-AN.

Kaptein's rules [27] predict the appearance of absorptive geminate polarization for the singlet precursor of the initial radical pair, and emission for the triplet precursor. Indeed, the  $g$  factors of the naphthoxyl and acetyl radicals are 2.0043 [28] and 2.0005 [29] respectively; the sign of the hyperfine interaction constants is negative for the 1 and 3 protons of 2-naphthoxyl and positive for the acetyl protons [30]. Thus the absorptive CIDNP observed on the methyl protons of 1-AN at 2.70 ppm confirms the singlet precursor of the parent radical pair.

The emissive polarization of 2-naphthol at 7.08 ppm and of ketene at 2.14 ppm can be accounted for in two different ways. First, if the polarization of these products is formed mainly in F pairs, this polarization would have an opposite sign with respect to geminate CIDNP. Another explanation is that the polarization of 2-naphthol and ketene is formed in the triplet radical pairs. The measurements of the CIDNP dependence on the quencher concentration and the time-resolved CIDNP experiments strongly support the latter assumption. The addition of the triplet quencher piperylene (about 0.01 M) decreases the intensity of emissive CIDNP and does not influence the absorptive polarization. The Stern-Volmer plot for the quenching of emissive CIDNP (Fig. 7) demonstrates a linear dependence with a slope of  $65 \pm 3 \text{ M}^{-1}$ .

The time-resolved CIDNP spectra, in addition to the steady state CIDNP signals described above, show a positive polarization at 2.32 ppm, which corresponds to the methyl protons of initial 2-NA (in the steady state CIDNP spectra, this polarization was hidden under the "dark" signal of the initial

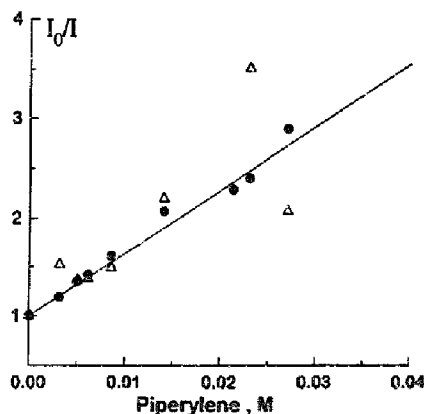


Fig. 7. Stern-Volmer plot of CIDNP intensities for ketene (circles) and 2-naphthol (triangles) vs. the piperylene concentration.

compound). Thus it can be concluded that, in this system, the singlet radical pairs can recombine to form the initial compound.

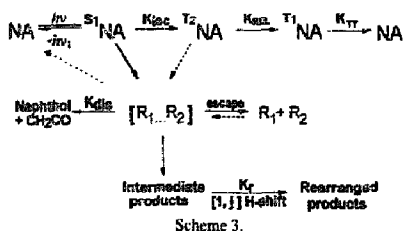
The time-resolved CIDNP spectra, obtained with zero time delay between the laser pulse and detection, indicate the presence of the emissive signals described above, which increase in intensity with increasing time. This means that the contributions to the formation of emissive CIDNP of geminate and homogeneous processes are of the same sign, which is in good agreement with the assumption about the triplet origin of this polarization.

Triplet or singlet radical pair formation is caused by a thermally activated crossing from bonding triplet or singlet excited states to the dissociative state [16]. The existence of such activation in the photolyses of aryl ethers has been reported [31–33]. In our steady state CIDNP experiments, an increase in absorptive CIDNP intensity with increasing temperature was observed in the case of 2-NA photolysis. The corresponding Arrhenius plot suggests that the activation energy of singlet radical pair formation is  $9.6 \pm 3 \text{ kJ mol}^{-1}$ , which is close to the value of  $15 \text{ kJ mol}^{-1}$  reported in Refs. [31,32]. The emissive CIDNP does not demonstrate a clear temperature dependence, which is probably due to the significant contribution of bulk processes to polarization formation.

The results obtained by different techniques, characterize the reaction from different sides. Studying the dependence of the product quantum yield on the piperylene concentration shows that product formation in the photolysis of both 1- and 2-NA takes place mainly from the excited singlet state. The weak influence of piperylene on the free radical quantum yield confirms this assumption, as well as the analysis of the CIDNP signs in the presence of piperylene.

At the same time, flash photolysis and CIDNP experiments reveal the involvement of two types of triplet state. The triplet states observed in laser flash photolysis experiments are non-reactive (the main source of decay in our conditions is triplet–triplet annihilation), whereas the triplets detected by CIDNP react giving rise to emissive polarization. The slope of the Stern–Volmer plot for the quenching of emissive CIDNP is  $75 \pm 5 \text{ M}^{-1}$  for 1-NA [7] and  $65 \pm 3 \text{ M}^{-1}$  for 2-NA in acetonitrile (cf. Figs. 4 and 7).

A comparison of the results obtained for 1- and 2-NA photolysis shows that the photo-Fries reactions of these compounds can be considered within the same general scheme (Scheme 3), but the contributions of the triplet radical pairs



to the reaction and their further transformations involving either recombination or disproportionation are different. In particular, in the photolysis of 1-NA, both the triplet and singlet precursors contribute to the formation of CIDNP on the methyl protons of the main reaction products [7], whereas, in the photolysis of 2-NA, the polarization of these products is created in singlet radical pairs only. In addition, ketene formation is less pronounced in the case of 1-NA photolysis, and the restoration of the initial compound in the reaction is detected only during the photolysis of 2-NA.

In Scheme 3, the following reaction steps can be distinguished:

1. radiation excites the NA parent molecule into the first excited singlet state, which can either dissociate to yield a radical pair or transfer to the upper triplet state; the singlet excited state is the main channel of product formation, but makes a small contribution to CIDNP;
2. most of the  $T_2$  triplet molecules relax to the  $T_1$  triplet state within a few nanoseconds; however, some dissociate to yield the same radical pair as that for the singlet precursor; this channel is of less importance (3%–5% for 1-NA [7] and 1%–2% for 2-NA), but is responsible for the observed emissive CIDNP effects;
3. the  $T_1$  triplet state of naphthyl acetate is non-reactive, its main channel of decay being triplet–triplet annihilation;
4. the in-cage recombination of radical pairs competes with the fast disproportionation and escape; the formation of ketene observed in the CIDNP spectra is more pronounced for 2-NA; escaped radicals decay in bulk reactions [17] and can also form the same radical pairs;
5. intermediate products undergo slow isomerization into the final products;  $k_f = (1.7 \pm 0.3) \times 10^4 \text{ s}^{-1}$  for the [1,3] hydrogen shift reaction for 1-NA.

Thus this detailed reaction scheme describes the experimental data obtained for both 1-NA and 2-NA photolysis. Further investigations of rearrangement reactions, including  $^{13}\text{C}$  CIDNP measurements, are in progress.

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## References

- [1] D. Bellus, *Adv. Photochem.* 8 (1971) 109, and references cited therein.
- [2] K.V. Sarkanen, C.H. Ludwig, *Lignins*, Wiley, New York, 1971.
- [3] J.C. Anderson, C.B. Reese, *Proc. Chem. Soc.* (1969) 217.
- [4] H. Shizuka, T. Morita, Y. Mori, T. Tanaka, *Bull. Chem. Soc. Jpn.* 42 (1969) 1831.
- [5] Y. Ohno, H. Shizuka, S. Sekiguchi, K. Matsui, *Bull. Chem. Soc. Jpn.* 47 (1974) 1209.

- [6] R. Nakagaki, M. Hiramatsu, T. Watanabe, Y. Tanimoto, S. Nagakura, *J. Phys. Chem.* 89 (1985) 3222.
- [7] N.P. Gritsan, Yu.P. Tsentelovich, A.V. Yurkovskaya, R.Z. Sagdeev, *J. Phys. Chem.* 100 (1996) 4448.
- [8] D. Elad, *Tetrahedron Lett.* (1963) 873.
- [9] H. Shizuka, T. Tanaka, *Bull. Chem. Soc. Jpn.* 41 (1968) 2343. H. Shizuka, *Bull. Chem. Soc. Jpn.* 42 (1969) 52.
- [10] H. Nozaki, R. Okada, R. Noyori, M. Kawanisi, *Tetrahedron* 22 (1966) 2177.
- [11] P.M. Miranda, A. Factor, *J. Polym. Sci. Part A* 27 (1989) 4427.
- [12] J.E. Herweh, C.E. Hoyle, *J. Org. Chem.* 45 (1980) 2195.
- [13] J.M. Lally, W.J. Spillane, *J. Chem. Soc., Chem. Commun.* (1987) 8. J.M. Lally, W.J. Spillane, *J. Chem. Soc., Perkin Trans. 2* (1991) 803.
- [14] J.W. Meyer, G.S. Hammond, *J. Am. Chem. Soc.* 94 (1972) 2219.
- [15] C.E. Kalmus, D.M. Hercules, *J. Am. Chem. Soc.* 96 (1974) 449.
- [16] S. Grimme, *Chem. Phys.* 163 (1992) 313.
- [17] E. Ghibaudi, A.J. Collusi, *Chem. Phys. Lett.* 94 (1) (1983) 121.
- [18] W. Adam, J.A. de Sanabia, H. Fischer, *J. Org. Chem.* 38 (1972) 2571. J.-K. Vollenweider, H. Fischer, *Chem. Phys.* 124 (1988) 333.
- [19] P. Subramanian, D. Greed, A.C. Griffin, C.E. Hoyle, K. Venkataram, *J. Photochem. Photobiol. A: Chem.* 61 (1991) 317.
- [20] C. Cui, R.G. Weiss, *J. Am. Chem. Soc.* 115 (1993) 9820.
- [21] Z. Wang, D.A. Holden, F.R.W. McCourt, *Macromolecules* 23 (1990) 3773.
- [22] C. Cui, X. Wang, R.G. Weiss, *J. Org. Chem.* 61 (1996) 1962.
- [23] D. Bellus, K. Schaffner, J. Hoigne, *Helv. Chim. Acta* 51 (1968) 1956.
- [24] Yu.P. Tsentelovich, H. Fischer, *J. Chem. Soc., Perkin Trans. 2* (1994) 729.
- [25] T. Arai, S. Tobita, H. Shizuka, *Chem. Phys. Lett.* 223 (1994) 521.
- [26] E.L. Allred, D.M. Grant, W. Goodlett, *J. Am. Chem. Soc.* 87 (1965) 673.
- [27] R. Kaptein, *J. Chem. Soc., Chem. Commun.* (1971) 732. K.M. Salikhov, Yu.N. Molin, R.Z. Sagdeev, A.L. Buchachenko, *Spin Polarisation and Magnetic Effects in Radical Reactions*, Elsevier, Amsterdam, 1984.
- [28] M. Adams, J. Blois, R.H. Sands, *J. Chem. Phys.* 28 (1958) 774.
- [29] J.E. Benett, B. Mile, *Trans. Faraday Soc.* 67 (1971) 1587.
- [30] H. Paul, H. Fisher, *Helv. Chim. Acta* 56 (1973) 1575.
- [31] S. Grimme, H. Dreeskamp, *J. Photochem. Photobiol. A: Chem.* 65 (1992) 371.
- [32] G. Pohlert, S. Grimme, H. Dreeskamp, *J. Photochem. Photobiol. A: Chem.* 79 (1994) 153.
- [33] G. Pohlert, H. Dreeskamp, S. Grimme, *J. Photochem. Photobiol. A: Chem.* 95 (1996) 41.