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The mechanism of oxidation of NADH analogues 5 Photooxidation of *N*-methyl substituted 1,4- and 1,2-dihydropyrimidines in the presence of quinones

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Abstract

The photoinduced interaction of the 1-methyl-4-phenyl-5-carbomethoxy-6-methyl-1,4(1,2)-dihydropyrimidines (1,4- and 1,2-DHPm) with quinones has been studied by means of CIDNP method in polar media. It was established that 1-methyl-4-phenyl-5-carboxymethyl-6-methylene-1,6-dihydropyrimidine (1,6-MDHPm) is a main reaction product. It has been found that radical cation of DHPm is more reactive species than earlier studied radical cations of related *N*-methyl substituted dihydropyridines and is disposed to proton loss resulting in neutral pyrimidinyl radical. The 1,6-MDHPm was formed by hydrogen atom loss from 6-CH_3 group of pyrimidinyl radical. Oxidation of the pyrimidinyl radical to pyrimidinium cation was not detected. Formation of pyrimidinium cation was detected in the presence of a high concentration of acetic acid in the reaction mixture.

Keywords: Dihydropyrimidines; Quinone; CIDNP; Photooxidation; Radicals; Radical ions

1. Introduction

Photooxidation of dihydropyridines (DHP) has attracted considerable interest as a model process of the NADH → NAD^+ transformation. Various physicochemical methods were used to establish the mechanism of this process [1]. Of special interest is the application of spin chemistry methods which provide the possibility to obtain unique information that cannot be obtained by other experimental techniques [2]. It was found that in all reactions of DHP with quinones, the primary stage is single-electron transfer process leading to an initial radical ion pair (RIP) [3–6], whereas the consecutive steps depend on the initial DHP structure. For *N*-unsubstituted DHP, the second step is N–H proton transfer from DHP radical cation to semiquinone radical anion. Resulting radical pair (RP) of nitrogen centered and neutral semiquinone radicals leads to pyridine as a main reaction product [4]. The *N*-alkyl substituted DHPs demonstrate a hydrogen atom transfer from DHP radical cation to neutral semiquinone radical leading to the formation of pyridinium cation as a reaction product [5]. The last mechanism also explains the origin of CIDNP effects observed during photooxidation of NADH by flavins [3]. The presence of acyl substituents in 3,5 position of the DHP ring provides for the autooxidation process where DHP molecule plays the role of electron donor in the excited state, and electron acceptor in the ground state [4]. For *N*-acyl substituted DHP, it was found that primary radical cation undergoes to C–N bond cleavage resulting in products different from those observed for *N*-alkyl substituted DHP [7]. These observations clearly demonstrate that the mechanism of the photooxidation of DHP in the presence of the electron acceptors depends on the substituent nature and includes the sequence of different radical stages.

From our perspective, it is interesting also to expand the research on the related compounds. The present study is devoted to the investigations on the photooxidation of substituted dihydropyrimidines (DHPm) by quinones aimed to clarify the influence of the ring structure change from DHP to DHPm on the reaction mechanism. Substituents of the DHPm were chosen the same as in earlier studied DHP [5] to verify the influence of the ring structure on the reaction mechanism. The reactions of both 1,4- and 1,2-DHPm were investigated.

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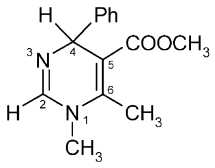
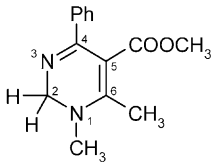
2. Experimental

2.1. Chemicals

N-Methyl-4-phenyl-5-carbomethoxy-6-methyl-1,4(1,2)-dihydropyrimidines (1,4- and 1,2-DHPm) were synthesized by desulfurization of the corresponding pyrimidine-2(1*H*)-thione and its 3,4-dihydroderivative with Raney nickel [8,9].



1,4-DHPm



1,2-DHPm

1,4-Naphthoquinone (1,4-NQ) was recrystallized from ethanol. The commercial deuterated solvent, CD_3CN (99.95–99.98% D, "Isotope" or CIL) was purified by distillation over P_2O_5. Perdeuteroacetic acid (99.5% D, Aldrich) was used as supplied. The fresh stock solution (5×10^{-3} M) of both DHPm and 1,4-NQ in the CD_3CN was prepared for each experimental series. For most of CIDNP experiments the sample was deaerated by bubbling of Ar for 15 min prior to irradiation. To check the multiplicity of radical pair precursor the samples were bubbling of pure oxygen for 15 min.

2.2. CIDNP

Samples in standard 5 mm Pyrex NMR tubes were irradiated directly in the probe of NMR spectrometer at room temperature. Time-resolved (TR) [10] and pseudo-steady-state (PSS) [11] CIDNP experiments were performed using DPX200 Bruker NMR spectrometer (200 MHz ^{1}H operating frequency, $\tau(90^\circ) = 10\,\mu s$). The Lambda Physik EMG 101 MSC excimer laser was used as a light source (308 nm, 15 ns, 100 mJ at output window and 20 mJ per pulse in the sample volume). For TR experiments, detection radio frequency pulse width was 4 μs, delay time between laser and detection pulses was varied from 0 to 10 000 μs. For PSS experiments the pulse sequence program included eight laser pulses per scan.

Quantum chemical and ESR data [12] were used to identify the paramagnetic intermediates formed in these reactions. The quantum chemical calculations of hyperfine coupling (HFC) constants were performed as follows. First, AM1 (HyperChem 5.02, Hypercube Inc.) as one of the most accurate semi-empirical quantum chemistry method was used for geometry optimization of the paramagnetic species. The HFC values for these optimized species were obtained by the INDO method specially parameterized for calculation of the magnetic properties of radicals [13]. The main feature of the used INDO method is the ability to annihilate the high-spin states. The method allows to get the average value of $\langle S^2 \rangle$ equal to 0.75 ± 0.01, which characterizes the free radical with spin $S = 1/2$. The above procedure provides more accurate magnetic resonance parameters data then those obtained by AM1 method (and its re-parameterization known as PM3 [14]), especially for conjugated π-systems [3,15].

The pre-saturation of the equilibrium NMR signals of initial compounds in TR and PSS experiments allows to observe only polarized signals [16]. Thus, one can establish the structure of the paramagnetic intermediates more definitely on the basis of comparison of the integral intensities of polarized lines (normalized per proton) with HFC constants (experimental or calculated) for the corresponding nuclei in the suggested radical—precursor of the polarized product.

3. Results

UV spectra of initial compounds in acetonitrile are presented in Fig. 1. Molar extinctions of 1,4- and 1,2-DHPm at 308 nm are 6.3×10^3 and 3×10^3 M^{-1} cm^{-1}, respectively. Absorption spectrum of reaction mixture is exactly the additive of the absorption spectra of initial compounds. This indicates that no charge transfer complexes in the ground state are formed on mixing of the reagents.

Figs. 2 and 3 present the NMR spectra of the reaction mixture (a) before and (c) after irradiation. In the present study, the change from the DHP to DHPm structural frame leads to the formation of the main product differing from the expected pyrimidinium cation analogously with previous investigations [3,5]. Photo-CIDNP spectra observed in the process under study are shown in Figs. 2 and 3b. Observation of the nuclear polarization of the main reaction product leads to conclusion about the formation of this product through radical pair stages. As one can see from Figs. 2 and 3, the same main product was formed for both 1,2- and 1,4-DHPm. The chemical shifts and the CIDNP effect signs of the initial compounds and the main product are presented in Table 1. Table 2 lists the observed CIDNP effects of the initial 1,4-NQ and its reduced form 1,4-naphthohydroquinone.

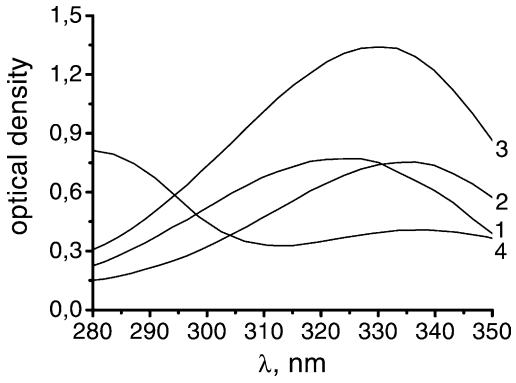


Fig. 1. UV spectra of the acetonitrile solutions: (1) 10^{-3} M of 1,4-DHPm; (2) 10^{-3} M of 1,4-NQ; (3) reaction mixture -10^{-3} M of both 1,4-DHPm and 1,4-NQ; (4) 10^{-3} M of 1,2-DHPm. Optical length 1 mm.

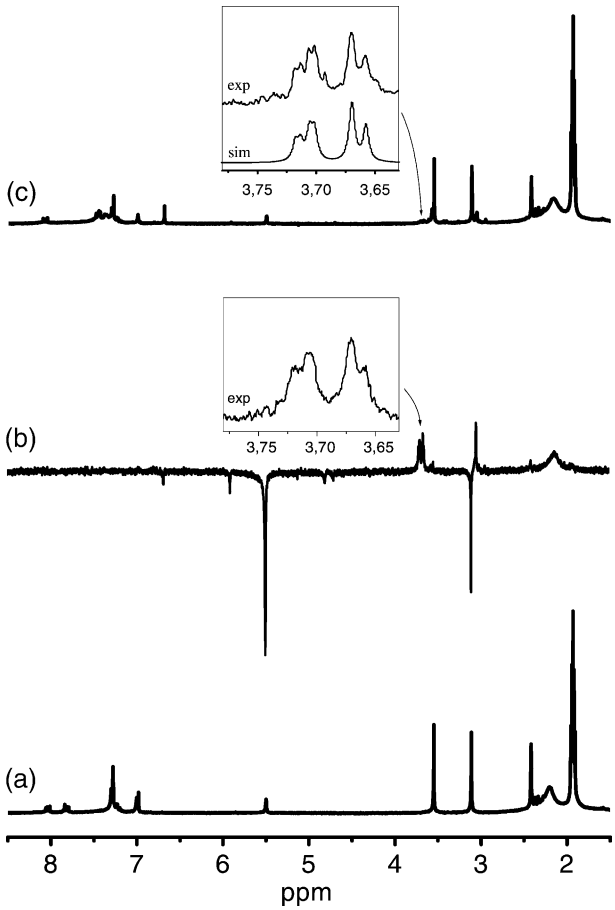


Fig. 2. NMR spectra of the reaction mixture of 1,4-DHPm (10^{-3} M) and 1,4-NQ (10^{-3} M) in deuteroacetonitrile: (a) before, (b) under and (c) after UV irradiation. Because of pre-saturation technique the CIDNP spectrum (b) contains only polarized signals. Inserts show the observed (b and c) and simulated (c) spectra of multiplet of terminal CH_2 protons.

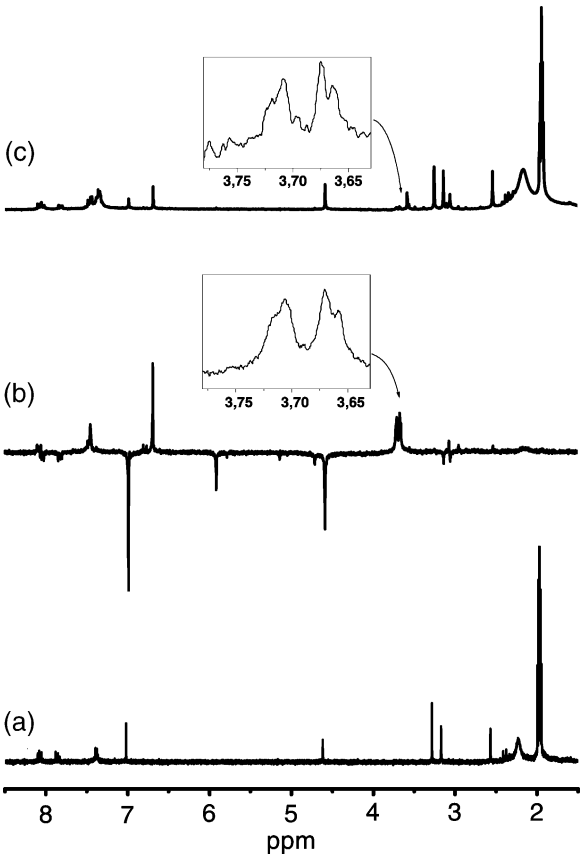


Fig. 3. NMR spectra of the reaction mixture of 1,2-DHPm (10^{-3} M) and 1,4-NQ (10^{-3} M) in deuteroacetonitrile: (a) before, (b) under and (c) after UV irradiation. Inserts show the observed spectra of multiplet of terminal CH_2 protons. All other conditions are the same as in Fig. 2.

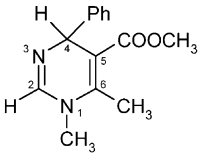
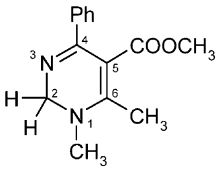
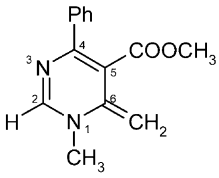
3.1. Product structure

The structure of the main product can be established from its NMR spectrum and corresponds to 1-methyl-4-phenyl-5-carboxymethyl-6-methylene-1,6-dihydropyrimidine (1,6-MDHPm). NMR spectrum indicates on the preservation of the 4-$COOCH_3$ and 1-CH_3 groups, and the absence of the 6-CH_3 group in the product. The multiplet structure at 3.7 ppm (frame in Fig. 2) was attributed to the terminal 6-CH_2 group. Its chemical shift is characteristic of this structural fragment and has a typical value of 3.7–4.0 ppm (for example, 3.70 and 3.99 ppm of CH_2 protons of the 1,3,3-triethyl-2-methyleneindoline [17]). The observed multiplet structure may be interpreted as AB part of ABX type of spectrum where $\Delta\delta_{AB} = 8.8$ Hz, $J_{AB} = 2.4$ Hz and $J_{AX} = 0.9$ Hz $\gg J_{BX}$. Simulated NMR spectrum for the above parameters is in a good agreement with the experimental one (frame in Fig. 2). The presence of the AB part clearly indicates that terminal 6-CH_2 protons have slightly different magnetic shielding. It is followed from the absence of the free rotation around a double bond and the influence of the carboxymethyl group on the shielding of closest proton of terminal double bond (1,6-MDHPm structure in Table 1). The typical value of the spin–spin splitting of terminal protons is about 2–3 Hz, and is in a good agreement with the value observed. The small spin–spin splitting constant of 0.9 Hz is characteristic for the remote interaction via four to five bonds in conjugated π-system. Because our AM1 calculation predicts the plane structure of 1,6-MDHPm, this splitting may be attributed to the interaction between one of the 6-CH_2 protons and 2-H proton of the ring. Chemical shift of 2-H proton is 7.45 ppm which is also a typical value.

3.2. Magnetic properties of intermediates

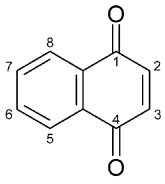
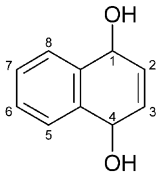
The HFC constants of all possible intermediates involved in the process under study were calculated. Table 3 shows the HFC constants of the 1,4- and 1,2-DHPm radical cations and these of the neutral pyrimidinyl radical as one of tentative paramagnetic intermediate. Isotropic HFC of 1-CH_3 and 6-CH_3 groups was obtained by averaging the calculated HFC values of all protons in CH_3 group. HFC constants of protons in carbomethoxy group have negligible values and are not included in Table 3.

Table 1
Chemical shifts and CIDNP effects of the initial DHPm and the main reaction product

Compound	^{1}H Chemical shifts of functional groups (ppm) and their CIDNP[a]				
	6-CH_3	1-CH_3	5-$COOCH_3$	4-H	2-H
	2.42 (no)	3.11 (E)	3.55 (no)	5.50 (E)	7.02 (no)
	2.53 (no)	3.13 (E)	3.24 (no)	–	4.59 (E)
 **1,6-MDHPm**	3.70 (A)	3.05 (A)	3.57 (no)	–	7.45 (A)[b]

[a] The CIDNP effects are given in parentheses.
[b] This polarization was observed only if initial reagent is 1,2-DHPm.

Table 2
Chemical shifts and CIDNP effects of the initial 1,4-NQ and 1,4-naphthohydroquinone

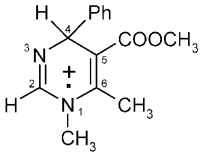
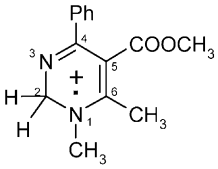
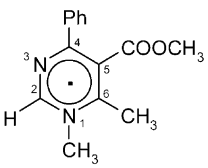
Compound	^{1}H Chemical shifts of protons (ppm) and their CIDNP[a]		
	2,3-H	5,8-H	6,7-H
	6.98 (E)	8.00 (E)	7.77 (E)
	6.68 (A)	8.07 (A)	7.51 (A)

[a] The CIDNP effects are given in parentheses.

4. Discussion

As it has been mentioned above, the main product of the process under study differs from the expected pyrimidinium cation in a parented reaction of 1,4-DHP. The structure of the main product corresponds to the 1,6-MDHPm for both 1,2- and 1,4-DHPm. This allows to suppose the existence of a unique product precursor. On the other hand, CIDNP effects of the initial DHPm protons, emission of 4-H (or 2-H) and 1-CH_3 group, are in a good agreement with the spin density distribution in the corresponding radical cation of DHPm, because these protons have the same sign and prevailing values of the HFC constants (Table 3). Under the assumption of the short-lived RIP, the expected polarization of different protons in the diamagnetic product is proportional to the number of these protons and their HFC values in radical cation [2,18]. Under our experimental conditions

Table 3
Calculated isotropic HFC constants (in Gauss) of tentative radical intermediates involved in the process

Intermediate	1-CH3	2-H	4-H	6-CH3
	9.6	1.5	56.9	−1.1
	5.5	52.5	–	−1.3
	3.3	−3.2	–	10

(polar solvent acetonitrile), this assumption is quite reasonable because following the calculation [19] and experimental results [20] it has been shown that a lifetime of radical ion pair in polar solvents resembles to those of a neutral radical pair. The expected ratio of CIDNP intensities based on calculated HFC values for 4-H and 1-CH_3 is 1.98 for 1,4-DHPm, and about 6.3 for 2-H and 1-CH_3 in 1,2-DHPm (Table 3). These values are in a good agreement with experimentally observed ratio between net CIDNP intensities (1.75 and 6.25 for 1,4- and 1,2-DHPm, respectively). Therefore, one might conclude that initial stage of the photo process is a single-electron transfer reaction resulting in the RIP of radical cation of DHPm and radical anion of 1,4-NQ. A back-electron transfer in this RIP results in the CIDNP effects observation of the initial compounds. CIDNP analysis according to Kaptein rules [21][1] gives the triplet multiplicity of the primary RIP (in-cage product, $\Delta g < 0$, HFC $>$ 0). As it has been shown in Section 2, under our experimental conditions the light is mainly absorbed by DHPm. The efforts to find the literature data on intersystem crossing (ISC) constant in DHPm were unsuccessful. Nevertheless, the related compounds have a quantum yield of ISC around 0.5–0.8 [22]. Also, it has been shown that a direct photolysis of the related dihydropyridines and acridans occurs from the excited triplet state [1].

Since HFC of 6-CH_3 in the DHPm radical cation is a negligible in comparison with the HFC for 1-CH_3 and 4-H for 1,4-DHPm or 2-H for 1,2-DHPm, the enhanced absorption of the 6-CH_2 in the 1,6-MDHPm indicates that this polarization cannot be formed in primary RIP. The presence of this polarization leads to assumption about existence of at least one more paramagnetic intermediate. Note that pyrimidinium cation as a possible product of primary RIP cannot be considered as the main product precursor, since, in this case, all polarization should be transferred from primary RIP [5]. For this reason, the intermediate structure should comply with the requirement of the largest HFC value of the 6-CH_3 protons. Among possible candidate this could only be pyrimidinyl radical where, according to our calculations, the protons of 6-CH_3 group have maximum HFC value (see Table 3). This assumption also correlates with the above suggestion of single precursor of the main product. Polarization in this case is formed in RP of pyrimidinyl and neutral semiquinone radicals. Disproportionation through hydrogen atom transfer from 6-CH_3 group of pyrimidinyl radical to semiquinone radical results in 1,6-MDHPm and 1,4-naphthohydroquinone. RP formation can occur (1) through consecutive RIP $\rightarrow$ RP, either (2) by direct hydrogen atom transfer from excited state of DHPm to 1,4-NQ or (3) by proton loss of free DHPm radical cation escaped from geminate recombination. The absence of a pronounced CIDNP time dependence allows to exclude the third pathway. If the main product is formed from the escaped DHPm radical cation, then it (and its polarization) should arise as a result of random encounters of radical cation and semiquinone radicals. The rate of encounter process is controlled by mutual diffusion of radicals. Taking into account that, in our case, energy of quantum of light is 6×10^{-14} mJ, one may estimate the radical concentration to be around 10^{-4} M. Using the well-known expressions for diffusion-controlled processes and estimated free radical concentration, one might conclude that expected free radical decay half-time is about 10–20 μs which is greater than time resolution of our experiments (2 μs). This estimation is close to other CIDNP results on the kinetics of escape product formation under similar experimental conditions (see, for example, [23]). For the above reasons it was concluded that formation of 1,6-MDHPm is a geminate process.

To clarify the origin of the 1,6-MDHPm polarization CIDNP experiments were carried out in deaerated and oxygen-saturated solutions. Oxygen is known to be an effective quencher of triplet excited states due to the triplet multiplicity of its ground state. If RIP and RP are formed simultaneously, they should have a different multiplicity, because, CIDNP analysis for RP of pyrimidinyl and neutral semiquinone radicals requires the initial singlet multiplicity of this RP ($\mu < 0$). If that is the case, the increase in the oxygen concentration should affect the relationship between pathways (efficiency decrease mainly for the T-RIP formation) and consequently relationship between polarization intensities of initial compound (DHPm) and main reaction product (1,6-MDHPm). Fig. 4 shows the effect of the presence of oxygen in the reaction mixture on photo-CIDNP spectra. In the oxygen-saturated samples, the polarization has decreased by factor of 2 as compared to the deaerated samples under the same experimental conditions. Nevertheless, the experimental ratios of integral CIDNP intensities of 4(2)-H of DHPm and 6-CH_2 of 1,6-MDHPm are nearly equal in both cases (0.25 ± 0.03 in the absence and 0.28 ± 0.03 in the presence of oxygen). Since oxygen did not change significantly the ratio between formation rates of

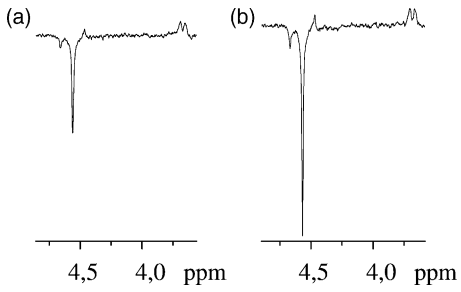


Fig. 4. TR photo-CIDNP spectra in the reaction of 1,2-DHPm and 1,4-NQ: (a) in the presence and (b) in the absence of oxygen in solution. All other conditions are the same as in Fig. 2.

[1] $\Gamma_{ne} = \mu \times \varepsilon \times \Delta g \times a \times \gamma$, where $\Gamma_{ne} > 0$ corresponds to enhanced absorption and $\Gamma_{ne} < 0$ to emission in ^{1}H NMR spectrum; $\mu > 0$ for triplet and $\mu < 0$ for singlet precursor of RP; $\varepsilon > 0$ for in-cage and $\varepsilon < 0$ for escape product of RP; Δg is the sign of difference between g-factor of radical which contains polarized nucleus and g-factor radical partner; a is the sign of HFC of polarized nucleus in radical; $\gamma > 0$ for recombination product in ground state and $\gamma < 0$ for product in triplet excited state (modification by G.L. Closs for radical ion pairs).

the DHPm and 1,6-MDHPm, one might conclude that both substances have the single precursor (T-RIP). Polarization of 1,6-MDHPm in this case is originated from consecutive RIP → RP and has contributions from both pairs. According to the theory the polarization of consecutive RP, recombination product should have two contributions: (a) from primary RIP with the polarization sign corresponded to escape product and (b) from consecutive RP [24]. Qualitatively, it has a simple explanation, i.e. proton transfer in geminate RIP is spin non-selective process and, thus, from this viewpoint, is equivalent to the escape process. As one might see from Figs. 2 and 3, CIDNP effects of 1-CH_3 of initial DHPm (emission) and 1,6-MDHPm (adsorption) are in agreement with those expected from theory. At the same time, polarization of the product of consecutive RP should be formed within the time-scale of geminate recombination, i.e. nanosecond time range. This explains why polarization of 1,6-MDHPm does not demonstrate any changes at microsecond time range (Fig. 5). The large polarization of 6-CH_3 protons in RP could be explained by the prevalent HFC values of the corresponding pyrimidinyl radical (see Table 3).

Scheme 1 shows the reaction mechanism based on the above reasons, and includes the following stages:

(a) single-electron transfer from DHPm to 1,4-NQ leading to RIP formation;
(b) in-cage proton transfer in RIP of 4-H from 1,4-DHPm (or 2-H of 1,2-DHPm) radical cation to 1,4-NQ radical

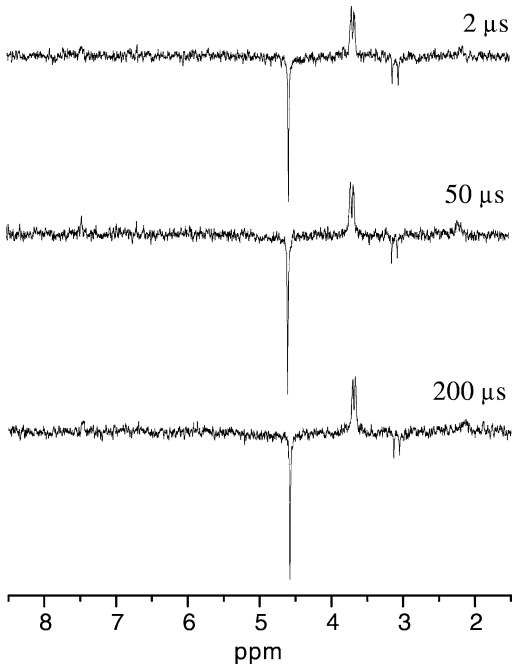
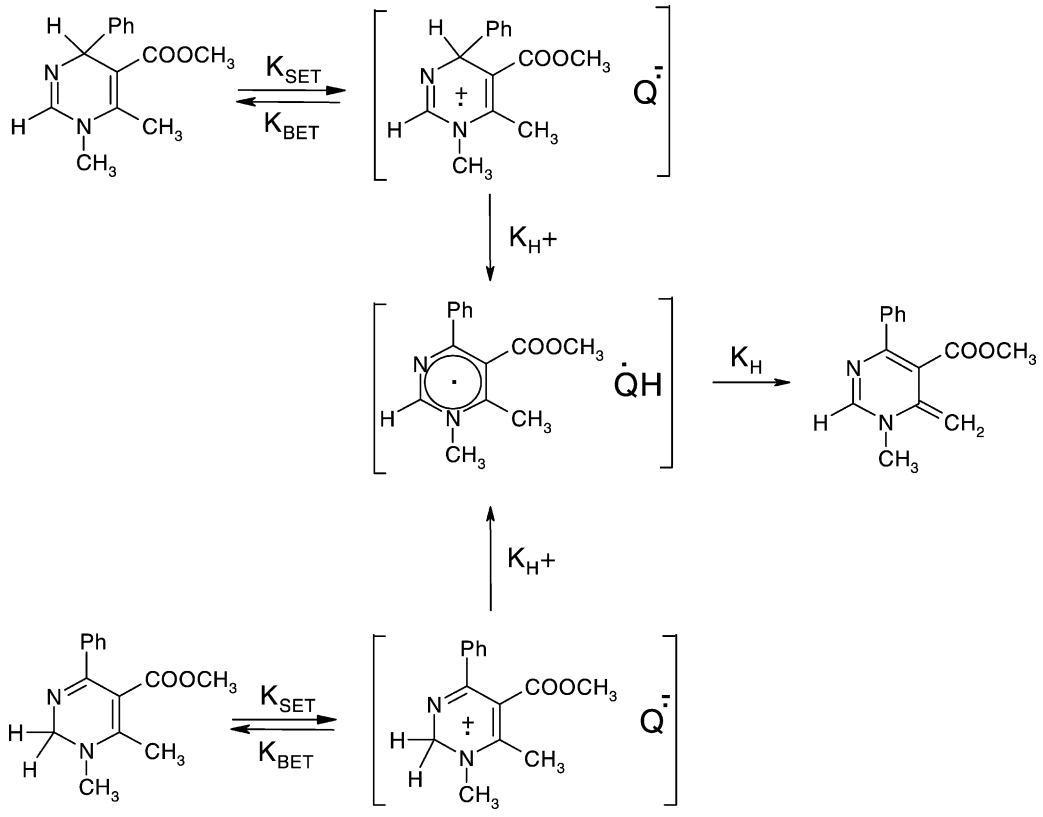


Fig. 5. TR photo-CIDNP time dependence in the reaction of 1,2-DHPm with 1,4-NQ. All other conditions are the same as in Fig. 2.



Scheme 1.

anion leading to neutral RP of pyrimidinyl and neutral semiquinone radicals;

(c) hydrogen atom transfer from 6-CH_3 group of pyrimidinyl to semiquinone radical resulting in 1,6-MDHPm and 1,4-naphthohydroquinone.

Scheme 1 is consistent with the observed CIDNP effects but, in general, CIDNP observation may not explicitly indicate that the radical mechanism is the prevalent reaction pathway. There is well-known example of the CIDNP observation in the formation of Grignard reagent where polarization reflects only a side reaction pathway [25]. To elucidate the contribution of radical pathway, the additional experimental evidence are necessary. Usually, the observation of the significant magnetic field effect could be evidence of the prevalence of the radical mechanism. But, in the present case, another way could be suggested to establish the main reaction pathway. The essence of the technique suggested is chemical modification of the reaction system so that reaction mechanism proposed on the basis of CIDNP could be altered as a result of introduction of additional reagents into the reaction mixture. One might assume that an additional reagent is capable to modify chemically the paramagnetic intermediates leading to the formation of another reaction products. In the reaction under study, the simplest way is to transform semiquinone radical anion to neutral semiquinone radical. It is known that interaction of semiquinone radical anion with acids is very fast process with diffusion-controlled rate ($k \geq 10^9\,M^{-1}\,s^{-1}$) [26]. If this transformation can be realized within the lifetime of primary RIP, it should suppress consecutive RP formation by transformation of primary RIP to pair of DHPm radical cation and neutral semiquinone radical.

The dependence of CIDNP spectra on the concentration of added perdeuteroacetic acid is presented in Fig. 6. As one can see from Fig. 6, in fact, in the presence of a high acid concentration, the CIDNP spectrum demonstrates polarization of initial DHPm and single reaction product different from 1,6-MDHPm. NMR spectrum of this product corresponds to pyrimidinium cation. The main feature of its NMR spectrum is large high field shift of 1-CH_3 (around 0.9 ppm) from initial positions in DHPm. This is connected with the mutual influence of ring current of aromatic pyrimidinium cation and of structure conversion 1-N from amine to imine on the 1-CH_3 protons shielding. Polarization of both initial DHPm and cation originates from RIP. Note also, that in the presence of high concentration of

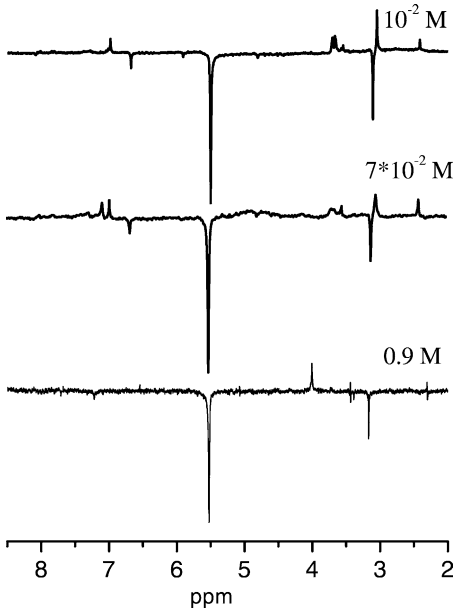
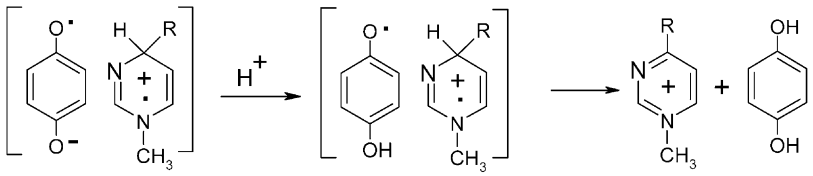


Fig. 6. PSS photo-CIDNP dependence in the reaction of 1,4-DHPm with 1,4-NQ on added perdeutero acetic acid concentrations. All other conditions are the same as in Fig. 2.

the acid the pyrimidinium cation is a single main reaction product. By analogy with the previous investigation of photooxidation of *N*-methyl substituted 1,4-dihydropyridines by quinones [5], it was assumed that the pyrimidinium cation formation occurs by hydrogen atom transfer from DHPm radical cation to neutral semiquinone radical (Scheme 2).

Influence of acid on the CIDNP spectra and the product yields leads to the conclusion on the reaction mechanisms established on the basis of CIDNP analysis as a main reaction pathway. In addition, from the acid influence on CIDNP spectra it is possible to estimate the time of RIP–RP transformation. Assuming that decrease of the 1,6-MDHPm polarization by a factor of 2 approximately corresponds to equivalent decrease in consecutive RP formation, and taking into account the acid concentration and rate constant of transformation of semiquinone radical anion to neutral radical, the time of the RIP–RP transformation was estimated as 5–10 ns. This estimation characterizes in-cage processes and additionally suggests the proposed reaction mechanism.



Scheme 2.

5. Conclusions

The detected transformation of primary RIP to RP indicates that the radical cation of DHPm is more reactive species than earlier studied radical cations of related *N*-methyl substituted dihydropyridines [5] and is disposed to proton loss resulting in neutral pyrimidinyl radical. Oxidation of the pyrimidinyl radical to pyrimidinium cation was not detected. The main reaction product (1,6-MDHPm) was formed by hydrogen atom loss from 6-CH_3 group of NAD-type pyrimidinyl radical. The presence of a high concentration of acetic acid in the reaction mixture leads to the formation of pyrimidinium cation. It has been found that the radical mechanism established by the CIDNP analysis basis is the main reaction pathway of the photoinduced interaction of DHPm with quinones in polar media.

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