

# Phototransformations of non-toxic antioxidants, the derivatives of 1,2-dihydroquinolines, in homogeneous and micellar solutions

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**ABSTRACT.** Reactions of transient species photogenerated from 6-R-2,2,4-trimethyl-1,2-dihydroquinolines (TMDQ) are very sensitive to medium variation. In anhydrous organic solvents, aminyl radicals were generated. They decay in the reaction of dimerization with the second-order rate constant decreasing in a row heptane > benzene > 2-propanol. When passing from organic solvents to water, methanol, and water-alcohol solutions, the kinetics and the direction of the reaction crucially change. As a result of the photolysis, the product of the addition of a solvent to the double bond of heterocycle, 4-hydroxy- or 4-methoxy-6-R-2,2,4-tetramethyl-1,2,3,4-tetrahydroquinoline is formed in water and methanol, respectively. The transformation is a complex reaction, and the formation of excited transient species is followed by a sequence of first-order and pseudo-first-order reactions. Unlike the photolysis in anhydrous organic solvents, the reaction in water and methanol does not involve aminyl radicals. In aqueous solutions, the first-order rate constants for the decay of transient species are higher in acidic and neutral solutions. At the pH close to  $pK_a$  of the transient species, it drops, indicating that the neutral form is less reactive. The same product is formed over the whole range of pH. For the anionic surfactant (SDS) in acidic and alkaline solutions, the apparent rate constant in the micellar solutions is lower than that in the aqueous (negative micellar catalysis). At the medium pH, a positive micellar catalysis is observed, and the rate constant of the decay depends linearly on the concentration of TMDQ in the micelles, indicative of the direct reaction between TMDQ and the cationic transient species.

## 1. INTRODUCTION

Effect of the medium on kinetics and mechanism of chemical transformations is one of the key problems of the modern physical chemistry. The polarity of a medium and hydrogen bonding between a reagent and a solvent play the most important role in this phenomenon. We have found earlier that the nature of a solvent affects the direction and kinetics of photolysis of 2,2,4,6-tetramethyl-1,2-dihydroquinoline (**1**) [1]. In this work, based on the identification of the product of the photolysis in water and methanol, we report the results of the kinetic examination of the reaction in methanol, which allows us to better understand the results obtained earlier for the photolysis of **1** in water and micellar solutions.

## 2. MATERIALS AND METHODS

2,2,4,6-Tetramethyl-1,2-dihydroquinoline (**1**) (Reakhim, Russia) was sublimed *in vacuo*. Methanol for spectroscopy (Merck) and bidistilled water were used. Azobisisobutyronitrile (AIBN) was successively recrystallized from benzene and ethanol.

Steady-state photolysis of solutions of **1** and other 1,2-dihydroquinolines was carried out with a DRSh-1000 mercury lamp using UFS-5 filter in quartz cells with a path length of 1 cm at the ambient temperature and at 45 °C.

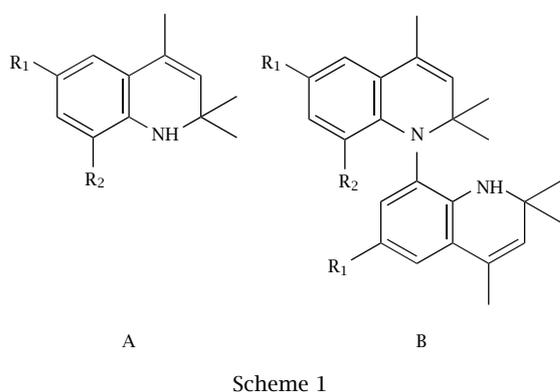
Absorption spectra in UV and visible regions were recorded with a Specord UV-vis spectrophotometer in quartz cells with a path length of 1 and 0.2 cm depending on the concentration of **1**.

Thermal generation of the radicals from **1** was carried out in the thermostatically controlled quartz cells with a path length of 1 cm in the cell compartment of Specord UV-vis spectrophotometer in the presence of the initiator of free radicals AIBN. The rate of initiation was  $2.5 \cdot 10^{-8} \text{ mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$ , [1]  $2 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$ , the temperature 45 °C, reaction time two hours. Consumption of **1** and formation of reaction products were followed by spectrophotometry and TLC. The solution of AIBN of the same concentration as in the working cell was used as a reference. When the reaction was accomplished, the reaction mixture was analyzed by TLC on silufol using a hexane: ether mixture 3 : 1 as an eluent and was compared with the mixture obtained upon photolysis. Flash photolysis experiments were carried out as described elsewhere [1].

## 3. RESULTS AND DISCUSSION

Substituted and partly hydrogenated quinolines of the general formula **A**, especially ethoxyquin ( $R_1 = C_2H_5O$ ,  $R_2 = H$ ), are widely used antioxidants and antiozonants for elastomers [2], for stabilization of vitamin A and  $\beta$ -carotene in feed, and to prevent the apples from scalding [3, 4]. During the photolysis of compounds **A** with  $R_2 = H$  in organic solvents (benzene, toluene, alkanes, propanol-2), the hydrogen atom breaks off from the molecule of dihydroquinoline, and an aminyl radical forms, which decays at the ambient temperatures predominantly in recombination reaction [5] giving 1-8 dimer **B** [6, 7] (Shceme 1).

The rate constants for the recombination of the transient radicals measured by flash-photolysis [5] and by



ESR [7] are close and equal to  $10^6$ – $10^7$   $M^{-1}s^{-1}$  depending on the nature of the substituent in position 6 and the solvent. The second-order rate constant decreases in a row of solvents heptane > benzene > 2-propanol and in a row of substituents  $R_1C_2H_5O > CH_3 > H$ . If  $R_2 \neq H$ , the rate constant for the radical decay drastically decreases, for instance, it is equal to  $10^2$   $M^{-1}s^{-1}$  for  $R_2 = CH_3$  [7].

In water, methanol, and water-alcohol (ethanol and 2-propanol) solutions the direction of the photolysis crucially changes. Upon the steady-state photolysis of A with  $R_1 = C_2H_5O, CH_3, OH,$  and H and  $R_2 = H$ , formation of the product different from the dimer is observed. The photolysis of the compound with  $R_1 = CH_3$  (1) was studied in detail. The absorption spectra registered in the course of the steady-state experiments (Figure 1) have isobestic points indicating that a single product is formed quantitatively upon the photolysis. The products formed in water and methanol 2 and 3, respectively, have absorption spectra similar in shape, but with different extinction coefficients.

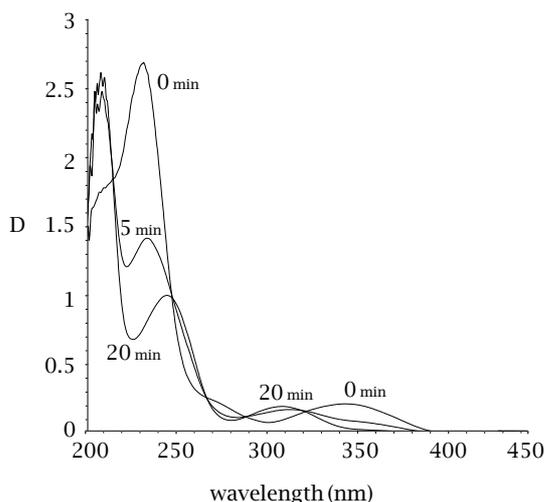
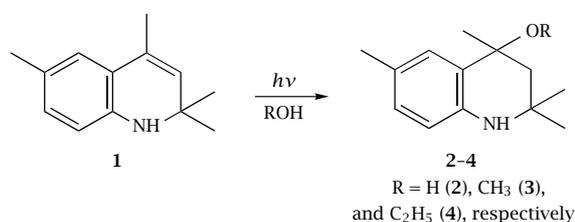


Figure 1. The changes in the absorption spectrum during the steady-state photolysis of 1 in methanol.

It worth noting that unlike methanol, the photolysis of 1 in anhydrous ethanol and 2-propanol occurs as in other organic solvent giving the dimer. As wa-

ter is added, the reaction of recombination of the transient aminyl radical changes the direction. It have been shown that in ethanol-water solution two products are formed, 2 and 4, with 2 being predominant. Therefore, different from compounds 2 and 3, compound 4 can be synthesized only in the mixture with 2 and even at the low concentration of water in the solvent its yield does not exceed 40%. When the water/ethanol ratio is 3 : 1, only compound 2 is formed.

The preparative-scale steady-state photolysis was carried out, products 2 and 3 were isolated and analyzed by  $^1H$  and  $^{13}C$  NMR, IR, and mass-spectroscopy [8]. The analysis of the structure of compounds 2 and 3 has shown that corresponding tetrahydroquinoline is formed as a result of the addition of solvent to the double bond of heterocycle. The phototransformation of 1 in water, methanol, and water-ethanol mixtures may be presented by Scheme 2:



Compounds 2, 3, and 4 are unstable and spontaneously converted into the parent dihydroquinoline in the dark. The rate of the conversion depends on the solvent, concentration, and weakly on the temperature [8].

As mentioned above, during the photolysis of 1,2-dihydroquinolines in organic solvents, aminyl radicals are the primary products, and they recombine giving dimeric products. The same products are formed when the reaction of hydrogen abstraction is induced thermally with initiators of radical reactions, for example, AIBN. In order to identify the nature of the transient species of the phototransformation in water and methanol, we compared a composition of the products of the steady-state photolysis of 1 in methanol and hexane at 45 °C and the products of the transformation of the radicals from 1, which were generated in methanol with the use of AIBN at the same temperature. Variations in the absorption spectra and TLC have shown that the composition of the products is close for the thermal reaction with initiator in methanol and the photolysis in hexane. At this temperature in addition to dimer, a small amount of 2,4,6-trimethylquinoline, product of the high-temperature conversion of the aminyl radicals, is formed. This compound has a characteristic absorption band with a fine structure in the range of 305–330 nm and thus can be easily identified [9]. Compound 3 was found neither by spectrophotometry (Figure 2, curves 1–7), nor by TLC. When the photolysis is carried out in methanol at 45 °C, the reaction goes as at the ambient temperature, is completed in half an hour, and gives only methoxy derivative 3 (Figure 2,

curve 8).

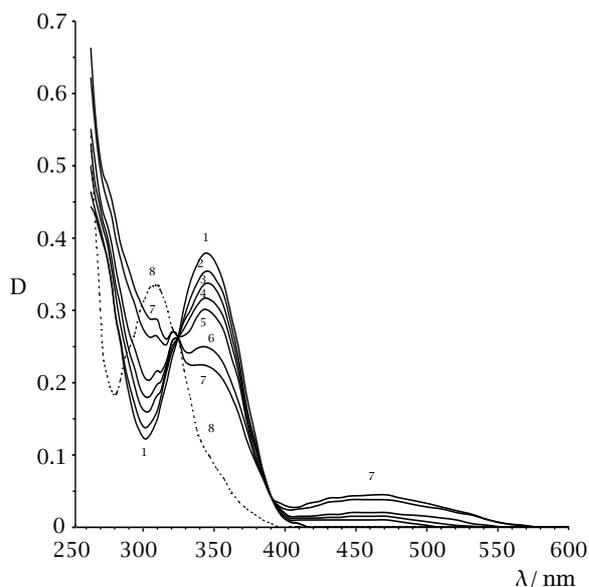
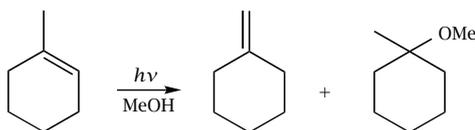


Figure 2. The changes in the absorption spectrum of compound **1** during initiated oxidation in methanol, initiator AIBN,  $w_i$   $2.5 \times 10^{-8} \text{ Ms}^{-1}$ , the reaction time (min): 0 (1), 15 (2), 30 (3), 45 (4), 60 (5), 90 (6), 120 (7); the product (8) of the photolysis of **1** in methanol;  $[1]$   $2 \cdot 10^{-4} \text{ M}$ ,  $45^\circ \text{C}$ .

The absence of **3** in the mixture of products of the induced thermal reaction cannot be rationalized in terms of a competition between the reaction of recombination of the aminyl radicals and the reaction of formation of compound **3**. If this competition took place at thermal initiation, it should also take place during the photolysis. Hence, the absence of compound **3** in the thermal reaction and dimer and quinoline, the products of conversion of the aminyl radicals, during the photolysis in methanol indicates that photolysis in methanol and oxidation initiated with AIBN goes *via* different transient species. It is also obvious that, the lowest triplet state does not take part in this reaction because the presence of oxygen have no effect on it.

Photoaddition of water and methanol have been studied intensely for the last three decades [10–13]. The photoaddition of methanol to 1-methylcyclohexene and relative compounds [10, 11] upon irradiation in the presence of an aromatic sensitizer (benzene, toluene, and xylene) are the closest to our system. This reaction is parallel to the formation of an exo-cyclic isomer (Scheme 3).



Scheme 3

The mechanism was suggested, which involved the formation of a carbonium ion, which converted either

in exo-cyclic isomer or added the solvent [10]. During the photolysis of 2-phenylbutadiene in methanol along with a dimer and 2-phenylbetene, different isomers with methoxy group were formed [12]. Unlike these compounds, in the case of dihydroquinoline **1**, the photoaddition of water and methanol goes practically quantitatively almost without formation of by-products. No sensitizer is necessary for this process.

Examination of decay traces at various wavelengths upon the pulse photolysis of **1** in methanol showed that the reaction was at least two-step (Figure 3).

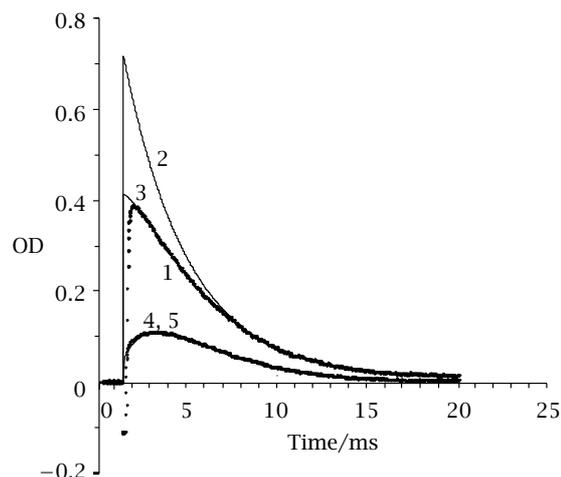


Figure 3. Experimental kinetic curves registered in the flash photolysis of **1** in methanol at (1) 420 and (4) 500 nm; (2) calculated exponential curve with  $k$   $290 \text{ s}^{-1}$ , (3) and (5) calculated fit curves with  $k_1$   $290 \text{ s}^{-1}$  and  $k_2$   $550 \text{ s}^{-1}$ .

At the wavelengths from 400 to 470 nm, only the decay was observed, but it was slower in the beginning than that exponential (compare curves 1 and 2). A kinetic curve registered at  $\lambda > 470 \text{ nm}$  showed a readily resolvable growth in the beginning followed with the decay (curve 4). The data over all range of wavelengths were processed in terms of two consecutive first-order reactions ( $\text{A} \rightarrow \text{B} \rightarrow \text{C}$ ) using a Microsoft EXCEL software according to the equation

$$\text{OD} = A_1 \exp(-k_1 t) - A_2 \exp(-k_2 t),$$

where OD is a measured optical density,  $A_1 = \varepsilon_A[\text{A}]_0 + \varepsilon_B[\text{A}]_0 k_1 / (k_2 - k_1)$ , and  $A_2 = \varepsilon_B[\text{A}]_0 k_1 / (k_2 - k_1)$ . In Figure 3, the examples of the fit of the experimental data to this equation are also given (curves 3 and 5). One can see that the calculations agree well with the experimental data, curves 1 and 4 practically coincide with 3 and 5. The calculated values of the rate constants are  $k_1$  ( $290 \pm 15$ )  $\text{s}^{-1}$  and  $k_2$  ( $550 \pm 50$ )  $\text{s}^{-1}$ . The rate constant for the first reaction is almost twice lower than that for the second reaction, and, in this case, that is the first reaction that is a limiting step for the overall process.

The effect of pulse intensity on the formation of the transient species was examined. Parameters  $A_1$  and  $A_2$ ,

which are proportional to  $[A]_0$ , were calculated at various wavelengths for different pulse intensities. A plot of calculated value of  $A_2$  given here, for example, at 500 nm as a function of the voltage applied to the pulse xenon lamp indicates that this process is biphotonic (Figure 4). It should be mentioned here that photolysis in organic solvents, which resulted in the formation of aminyl radicals, is a monophotonic process.

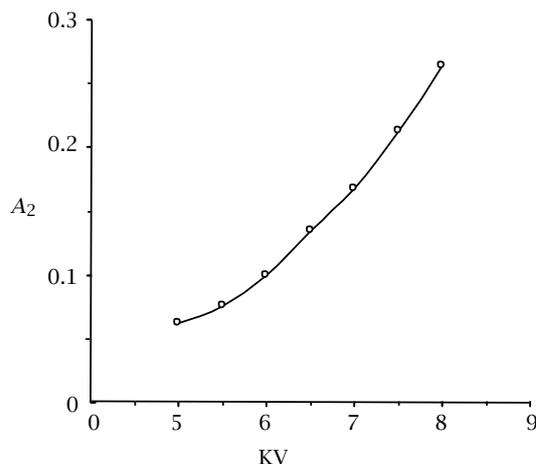


Figure 4. Parameter  $A_2$  calculated from the fit to the kinetic curves registered at 500 nm at different pulse intensities.

Based on the results obtained in this study, we can revise our previous results on the photolysis of **1** in aqueous and micellar (SDS) media [1, 14]. In those works, it was assumed that the transient species generated in these media were aminyl radicals and radical cations. Now we know that this is not so. Different from methanol, the decay curves in water and SDS micelles with exception for the very beginning fit well the one-exponential kinetics. The rate constants obtained from these curves depending on pH are from one to two orders of magnitude lower than those obtained for methanol. That is why, in this case, the first reaction is no longer a limiting step and manifests itself only in the very beginning as a deviation in the higher direction from the exponential law [1]. The measured first-order rate constant is the rate constant for the second step. In water, this rate constant are higher at the pH < 9.0, where the transient species is in the cationic form ( $25 \text{ s}^{-1}$  at pH < 9.0 and  $3.7 \text{ s}^{-1}$  at pH = 13.3), indicating that the transient cation is more active in this reaction. The decrease in the rate constant in water in comparison to methanol is consistent with the higher nucleophilicity of the latter [13].

In micellar solutions of SDS, different types of micellar catalysis were observed depending on pH. In the pH range from 3 to 10, the first-order rate constant increases linearly with the concentration of **1** in micelles indicative of the direct reaction of **1** with the transient cation in micelles [1, 14]. This reaction is parallel to the reaction of water with this transient, and it becomes predominant with concentrating of **1** in micelles.

A second-order rate constant of this process was determined and equal to  $(200 \pm 10) \text{ M}^{-1} \text{ s}^{-1}$  [1, 14]. Upon the steady-state photolysis in the micellar media, the spectrum of the final product is somewhat different from that obtained in water and contains a shoulder in the range of the absorption of compound **1** at 350 nm. This is one more evidence for the existence of the reaction of the addition of **1** to the transient cation.

At pH < 3 and pH > 11, the negative micellar catalysis is observed, *i.e.*, the rate constant decreases with increasing concentration of **1** in micelles. This means that the reaction of the addition of **1** to the transient species does not occur under conditions, when both particles are either cations or neutral. In these cases, the increase in the concentration of **1** in micelles leads to a decrease in the concentration of water in them and, consequently, to a decrease in the apparent first-order rate constant of the reaction of water addition.

Thus, the product and flash photolysis studies have shown that as a result of the photolysis of 6-R-2.2.4-trimethyl-1,2-dihydroquinolines in water, methanol, water-alcohol, and micellar solutions, the products of addition of the solvent or parent dihydroquinoline to the double bond of heterocycle are formed, corresponding 1,2,3,4-tetrahydroquinolines. The formation of the final product is a two-step reaction, and the generation of the first transient species is a biphotonic process. The study of the detailed mechanism of the reaction and the nature of the transient species is in progress.

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