ISSN 0023-1584, Kinetics and Catalysis, 2008, Vol. 49, No. 2, pp. 218–225. © MAIK "Nauka/Interperiodica" (Russia), 2008.
Published in Russian in Kinetika i Kataliz, 2008, Vol. 49, No. 2, pp. 231–238.

Photolysis of 1,2-Dihydroquinolines in Micellar Solutions of Anionic and Cationic Surfactants[1]

T. D. Nekipelova

Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, 119334 Russia
e-mail: nekip@sky.chph.ras.ru

Received February 15, 2007

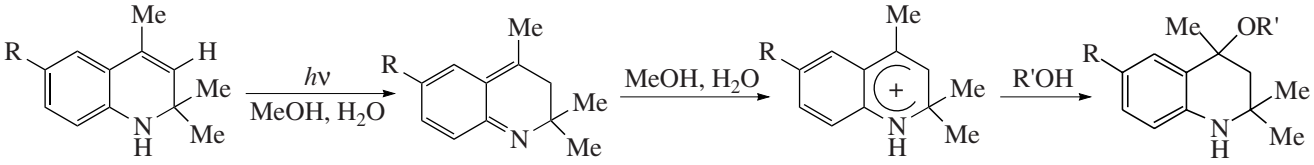
Abstract—The kinetics of the photolysis of substituted 1,2-dihydroquinolines (DHQ) in micellar solutions was studied by steady-state and flash photolysis. The photolysis mechanism depends dramatically on the location of DHQ molecules in micelles, which is governed by the surfactant nature. In micellar solutions of the anionic surfactant sodium dodecyl sulfate (SDS), where the DHQ molecules are located in the Stern layer, the intermediate species decay kinetics follows a first-order law. When DHQ is in neutral form (pH 4–12), the rate constant of the intermediate carbocation decay increases from 25 to 198 s^{-1} with an increasing concentration of DHQ in micelles. The positive micellar catalysis is caused by the acceleration of the final product formation with the DHQ molecule via proton abstraction from the intermediate cation. The formation of several types of intermediate species—carbocations in the aqueous phase and aminyl radicals in micelles—is observed in micellar solutions of the cationic surfactant cetyltrimethylammonium bromide (CTAB) due to the preferential location of DHQ molecules in the micellar core. The carbocation decays via a pseudofirst-order reaction with a rate constant close to that in the aqueous solution. The lifetime of the DHQ aminyl radicals in the micellar solutions is longer by several orders of magnitude than the lifetime observed for homogeneous solutions of hydrocarbons and alcohols.

DOI: 10.1134/S0023158408020080

In the mid-1990s, there was a small series of investigations focused on the specific features of the photolysis of 2,2,4,6-tetramethyl-1,2-dihydroquinoline in micellar solutions of anionic and cationic surfactants [1, 2] and on the dependence of the kinetic behavior of this compound in micelles of the anionic surfactant sodium dodecyl sulfate (SDS) on the acidity of the medium [3]. These studies were stimulated by the specifics of the antioxidation behavior of 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (ethoxyquin), one of the most efficient antioxidants of the dihydroquinoline series: unlike most antioxidants of other classes, ethoxyquin does not lose its activity in micellar solutions [4]. Moreover, the stoichiometric inhibition factor is larger in micellar solutions. The interpretation of the kinetic data obtained in [2, 3] was carried out under the assumption that the mechanism of the photolysis of dihydroquinolines in aqueous and micellar solutions is the same as in organic solvents; i.e., in aqueous solutions, as in organic solvents, the aminyl radicals are the primary photolysis products, which result from the homolytic cleavage of the N–H bond of the heterocycle [5].

Detailed studies of the photolysis mechanism for 2,2,4-trimethyl-1,2-dihydroquinolines (DHQ) with alkyl and alkoxy substituents in the C(6) and C(8) positions of the aromatic ring showed that the reaction mechanism in water and methanol is radically different [6–8]. In these solvents, no aminyl radicals are generated under irradiation and the primary photochemical reaction is double proton transfer from the water or methanol molecule to the excited singlet DHQ molecule (S_1) in the C(3) position of the heterocycle and from the N–H bond to the solvent (Scheme 1). This reaction yields cyclic *o*-quinomethane imine. Formally, this reaction is enamine–imine tautomerization, which takes place only in the excited state in the case of the DHQs examined. Cyclic *o*-quinomethane imine thus generated is protonated with the solvent to give a carbocation. This carbocation is subjected to nucleophilic attack by alcohol or water to afford the corresponding tetrahydroquinolines. The photochemical step of the reaction occurs only with the participation of water and methanol, but other alcohols with normal structure can participate in the nucleophilic reaction.

[1] This article was translated by the author.



Scheme 1. Mechanism of DHQ photolysis in aqueous and alcoholic solutions.

In this work, new data are analyzed and earlier results concerning DHQ photolysis in micellar solutions are revised taking into account the detailed mechanism of DHQ photolysis in different solvents. Note that the main body of the experimental results obtained in [2, 3] does not contradict the DHQ photolysis mechanism established later. Moreover, it became possible to correctly interpret those data whose previous interpretation in terms of the homolytic cleavage of the N–H bond with the formation of aminyl radicals and radical cations did not provide an understanding of some kinetic features of the reaction, namely, the micellar catalysis of intermediate species decay in SDS by increasing DHQ concentrations [2, 3] and the multicomponent kinetics of the intermediate species decay in the cationic surfactant cetyltrimethylammonium bromide CTAB [2]. Along with the results for the photolysis of 2,2,4,6-tetramethyl-1,2-dihydroquinoline (**1**) obtained earlier and in this study, new data on the photolysis of 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (**2**, ethoxyquin) and 6-ethoxy-1,2,2,4-tetramethyl-1,2-dihydroquinoline (**3**) in CTAB micellar solution are presented here. Besides the practical importance of ethoxyquin as an effective nontoxic antioxidant [9–12], the other reason why we chose this DHQ is that the intermediate species generated in its photolysis in protic solvents are substantially less active than in the case **1** [7]. The formation of aminyl radicals is impossible for compound **3**, and its photolysis in water and methanol occurs via the formation of a carbocation as a primary intermediate species with subsequent nucleophilic attack by the solvent. A comparison of the behaviors of these compounds in CTAB micellar solutions allowed the photolysis mechanism to be explained in terms of different locations of intermediate species in micelles.

EXPERIMENTAL

Starting chemicals. 2,2,4,6-Tetramethyl-1,2-dihydroquinoline (**1**) (Reakhim) was purified by vacuum sublimation. 6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (**2**) was purified by vacuum distillation. 6-Ethoxy-1,2,2,4-tetramethyl-1,2-dihydroquinoline (**3**) was synthesized by E.N. Khodot (Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences) by the N-methylation of compound **2**. Sodium dodecyl sulfate (SDS) (Reakhim) was twice recrystallized from EtOH. Cetyltrimethylammonium bromide (CTAB) (SERVA) was used without additional purification. Doubly distilled water was used in the preparation of micellar solutions.

Flash photolysis. The absorption spectra and decay kinetics of short-lived intermediate species were measured using a flash photolysis setup with a time resolution of 10 μs. Samples were irradiated in quartz cells with an optical path length of 20 cm by a xenon lamp with a pulse energy of 150 J. Variations in absorbance were registered with a system consisting of a Xe lamp (75 W), a ZMP-3 monochromator, a photomultiplier, and an oscilloscope based on a PCI Bordo 211 digital array and a PC. To excite the long-wavelength absorption band of DHQ, the excitation light was passed through a UFS-5 filter with a transmission range from 300 to 400 nm and maximum transmission at 365 nm. Intermediate absorption was recorded in the wavelength range from 400 to 600 nm in 10-nm steps.

The processing of the experimental data obtained in the flash photolysis experiments was carried out by global kinetic analysis. In this method, all experimental time profiles of absorbance, recorded at different wavelengths for the same solution, are approximated by the same integral kinetic equation with the absorbance and the rate constants as fitting parameters. The latter should be the same for the curves recorded at all wavelengths because they refer to the same reactions and the absorbances at different wavelengths characterize the absorption spectra of the corresponding intermediate species.

Steady-state photolysis was carried out by irradiation with a DRSh-1000 mercury lamp. The long-wavelength absorption band of DHQ was excited by light with a wavelength of $\lambda > 300$ nm using a UFS-5 filter. UV and visible absorption spectra were recorded in a Shimadzu UV-3101 PC spectrophotometer in quartz cells with an optical path length of 1 cm.

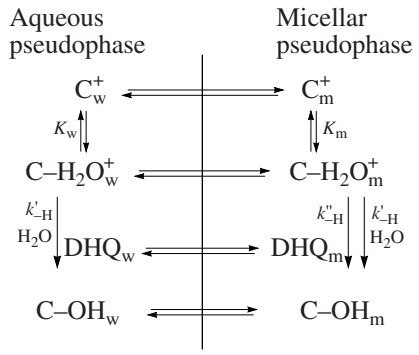
RESULTS AND DISCUSSION

In the anionic surfactant SDS, the DHQ molecules are located in the Stern layer. The solubilization of the DHQ molecules in the cationic surfactant CTAB begins from the micellar core, and, as the DHQ concentration increases, the solubilized molecules are located progressively more closely to the micellar periphery [1]. The different locations of the DHQ molecules in the SDS and CTAB micelles lead to a strong dependence of the reaction kinetics on the surfactant nature. For this reason, the specific features of DHQ photolysis in different surfactants will be considered separately. Since

the measured lifetimes of the intermediate species in water and methanol are on the millisecond timescale [7, 8] and are several orders of magnitude higher than the characteristic lifetime of exchange between micelles, the kinetic behavior of these species in micellar solutions should be described in the framework of the pseudophase model, which has been well developed for such cases [13–15], with the use of data available on DHQ phototransformations in water and water–alcohol mixtures [6–8, 16, 17].

DHQ Photolysis in Micellar Solutions of the Anionic Surfactant

The steady-state photolysis of **1** in the SDS micellar solutions is similar to photolysis in aqueous solutions: the quantitative formation of product characterized by a UV spectrum similar to the spectrum of the hydroxy adduct formed in water (λ_{max} = 305, 245, and 214 nm) [6] is observed. Qualitatively, the kinetic regularities of the reaction and the intermediate species generated in the flash photolysis are similar to those observed in water: intermediate species decay is a pseudofirst-order reaction, and the intermediate species structure depends drastically on pH. At 1 < pH < 12, the intermediate species generated by photoexcitation has the absorption spectrum of a carbocation (λ_{max} = 490 nm). In SDS micellar solutions with pH > 4, as distinct from aqueous solutions, the decay rate constant of this intermediate depends on the DHQ concentration in the micellar phase. It increases from 22 in aqueous solutions to 198 s^{-1} in the SDS micellar solutions as the concentration of **1** is increased (positive micellar catalysis) [3]. In solutions with pH < 4, the generated carbocation decays with a rate constant close to that in water. At pH > 12, as in the case of alkaline aqueous solutions, the formation of *o*-quinomethane imine is observed (λ_{max} = 420–430 nm). However, its lifetimes in these solutions are slightly longer than those in the aqueous alkaline solutions and the decay rate constant of this species increases with an increase of the concentration of **1** in micelles, as in the case of lower pH.



C^+ is the carbocation, $C–H_2O^+$ is the intermediate cation, C–OH is the final photolysis product, and the indices w and m refer to the aqueous and micellar phases, respectively

Scheme 2. Mechanism of carbocation transformations in the micellar solution.

Positive micellar catalysis at pH > 4 suggests that there is a reaction between DHQ and the carbocation or the product of its association with water and that this reaction yields the same final product as in water. In the aqueous solution, this reaction is not manifested because of the low concentration of both reactants. By a detailed study of the addition of water and alcohols to the carbocation [16, 17], it was found that the nucleophilic addition of a solvent to the carbocation generated from DHQ is accelerated by reagents capable to accept a proton. This is due to the formation of a positively charged complex between the carbocation and the protic solvent (intermediate cation), which converts into the final product via proton elimination. The presence of a compound with a proton affinity higher than the proton affinity of water accelerates the reaction. The DHQ concentration in micelles is many times higher than that in the aqueous phase, and the positive micellar catalysis in this case may be caused by the ability of the parent DHQ to accept a proton and thus accelerate the conversion of the intermediate cation into the final product. At pH < 4, the DHQ molecules (pK_a = 3.4) are protonated in aqueous solutions and are no longer proton acceptors. As a consequence, there is no micellar catalysis in this pH range. The mechanism of the carbocation transformations in the micellar solution within the framework of the pseudophase model is presented in Scheme 2.

In the micellar phase, this mechanism is similar to the mechanism of the nucleophilic addition of water to the carbocation in the H_2O–*i*-PrOH mixtures, when only one intermediate cation results from the interaction of the carbocation with water and two reagents—water and *i*-PrOH in the case of the water–alcohol solution and water and DHQ in the micellar phase—participate in the deprotonation reaction. As was mentioned above, the reaction with DHQ is insignificant in the aqueous phase because of the low DHQ concentration.

It is worth noting that there can be one more reaction of DHQ with the intermediate carbocation that will not change the kinetic regularities of the reaction. This is the nucleophilic addition of DHQ yielding a dimer. The absorption spectrum of this dimer would have bands typical of both tetra- and dihydroquinolines. However, as a result of the photolysis of DHQ in the SDS micellar solutions, the product forming quantitatively has a spectrum typical of tetrahydroquinolines. This allowed us to ignore this reaction.

The pseudophase model of bimolecular reactions involving ions and neutral molecules (the pseudophase model of ion exchange) [13, 14] is inappropriate for the description of the results obtained because it assumes that the reaction is pseudofirst-order with respect to its molecular component and the ionic component (usually a counterion) is in excess. In the case of DHQ at

pH 3–12, another situation takes place: the cation is the object of the kinetic study, and the parent neutral DHQ is in excess. For this case, an adequate description of the observed results was obtained in the framework of the simple pseudophase model under the assumption that the concentrations of the cation and DHQ in micelles depend on their partition coefficients P_1 and P_2, respectively, with Coulomb and hydrophobic interactions determining P_1 and only hydrophobic interactions determining P_2. In [2, 3], it was assumed that the cationic species is a radical cation, not a carbocation, as was demonstrated later. However, this does not change the formal kinetic regularities observed experimentally. Therefore, the dependence of the observed decay rate constant for the intermediate species (k_{obs}) on the DHQ and SDS concentrations derived in [2, 3] can be used in the analysis of experimental data obtained by flash photolysis for the SDS micelles:

$$k_{obs} - k_w = k_2[DHQ]_0 P_1 P_2 CV/(1 + CVP_1)(1 + CVP_2), \quad (1)$$

where k_w is the pseudofirst-order rate constant of the reaction of the carbocation with water in the aqueous phase, $C = [SDS] - cmc$, cmc is the critical micelle concentration, $V = 0.14$ l mol^{-1} is the molar volume of the Stern layer in which the reaction occurs, and the target rate constant is $k_2 = (200 \pm 10)$ l mol^{-1} s^{-1}. This constant, whose meaning is uncertain in [2, 3], characterizes the reaction of DHQ with the intermediate cation yielding the final reaction product.

DHQ Photolysis in the Micellar Solutions of the Cationic Surfactant

The change in the location of the DHQ molecules in the solutions of the cationic surfactant CTAB makes the photolysis kinetics of DHQ **1**–**3** very different from the photolysis kinetics in the aqueous and micellar SDS solutions (Fig. 1). The decay kinetics of the intermediate absorption is complex and corresponds to the formation of several intermediate species, the transformations of which occur independently according to different mechanisms with lifetimes varying from several milliseconds to several seconds. An adequate approximation of the experimental data for compounds **1** and **2** was obtained on the assumption that three intermediate species participate in the process, two species decaying in a first-order reaction and one species decaying in a second-order reaction:

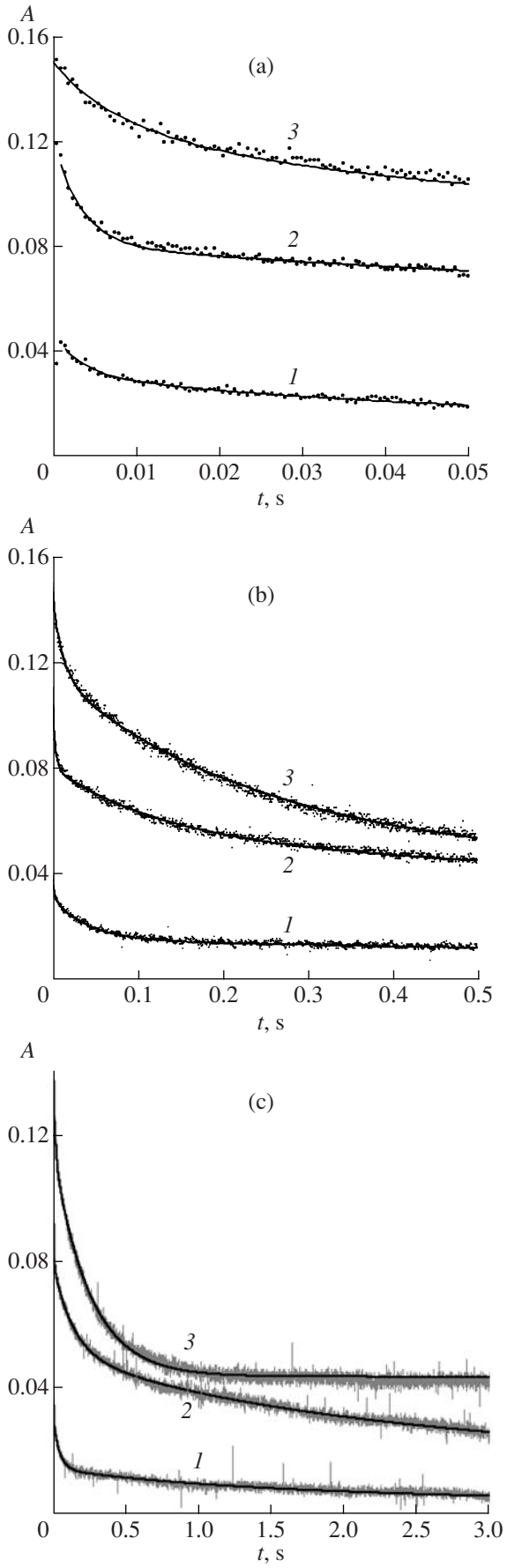
$$A^\lambda = A_1^\lambda \exp(-k_1 t) + A_2^\lambda \exp(-k_2 t) + A_3^\lambda/(1 + 2A_3^\lambda k_3 t/\varepsilon_\lambda l). \quad (2)$$

An adequate approximation for **3** was obtained on the assumption that four intermediate species participate in the reaction, three species decaying in first-order reactions with different rate constants and the concentration of the fourth species being almost constant during the longest registration period (5 s):

$$A^\lambda = A_1^\lambda \exp(-k_1 t) + A_2^\lambda \exp(-k_2 t) + A_3^\lambda \exp(-k_3 t) + A_4^\lambda. \quad (3)$$

In Eqs. (2) and (3), A^λ is the total absorbance registered at the wavelength λ, A_i^λ is the initial absorbance of the intermediate species i at the registration wavelength (the set of A_i^λ values at different wavelengths is the absorption spectrum of the species i), k_i is the decay rate constant for the species i, l is the optical path length, and ε_λ is the molar absorption coefficient of the species at the registration wavelength. Equation (2) suggests that the decay of the third intermediate occurs via a recombination reaction. In flash photolysis experiments, bimolecular rate constants are determined with a factor of $1/\varepsilon_\lambda$; that is, the calculated parameter is $2k_3/\varepsilon_\lambda$. Usually, ε_λ is determined from independent experiments. In this study, ε_λ in the CTAB micellar solutions was not determined, and the values of $2k_3/\varepsilon_\lambda$ were compared with the corresponding parameters obtained for hydrocarbon solutions [5, 18] assuming that ε_λ does not change significantly in micellar solutions.

The values of the rate constants and of the parameter $2k_3/\varepsilon_\lambda$ in the absorption maximum of the corresponding intermediate species, calculated by means of the global kinetic analysis of the experimental data according to Eqs. (2) and (3), are listed in the table, and the absorption spectra of the intermediate species are plotted in Fig. 2. Note the relatively large deviations in the parameter $2k_3/\varepsilon_\lambda$ as a function of the CTAB concentration. This parameter decreases by 30% as the CTAB concentration is reduced from 0.01 to 0.005 mol/l and does not change as the CTAB concentration is further decreased. This may be due to the change in the parameters of CTAB micelle formation because it is known that, as the CTAB and solubilizate concentrations change, the cmc value and the number of molecules forming a micelle also change [19]. At the same time, the deviations of the values of the first-order rate constants k_1 and k_2 in different runs do not exceed 5% and are independent of the DHQ concentration, k_2 being slightly higher than the rate constant for the corresponding carbocation in water k_w (table). The absorption spectrum of the species A_2 (Fig. 2a, curve *1*) for compounds **1**–**3** coincides with the spectrum of the carbocation with $\lambda_{max} = 480$ nm [7]. The concentration of the resulting carbocations increases with a decrease in the CTAB concentration and, accordingly, with an increase in the DHQ concentration in the aqueous phase. As follows from these results, most of the carbocation is generated and decays in the aqueous phase. The independence of k_2 of the DHQ concentration indicates the absence of micellar catalysis in the CTAB micelles, which is a consequence of the low DHQ concentration in the aqueous phase. On



the other hand, one could expect that the carbocation might give an adduct with Br^- in addition to the hydroxy adduct in the CTAB micelles. However, the independence of the k_2 values of the CTAB concentration indicates that the contribution from this reaction is low, which is in agreement with low nucleophilicity of Br^- [20].

The absorption spectra of the two other intermediate species (A_1 and A_3) for either of compounds **1** and **2** are almost the same and have λ_{max} near 430 (**1**) and 450 nm (**2**) (Fig. 2a, curves *2*, *3*). This allows us to assume that these species are chemically the same and the difference between their reactivities is due to their different locations in the micelle. The equality of k_1 values for all DHQ, including **3**, at all CTAB concentrations indicates that this rate constant is defined to a larger extent by the specific features of the processes occurring in the micellar phase rather than by the reactions of the corresponding intermediates as such. Two relaxation times were determined for micellar solutions by different methods [21]. One was attributed to the exchange between surfactant molecules of different micelles and had a value of 10^{-6}–10^{-4} s, and the other is determined by the lifetime of a micelle as a whole entity and has a value of ~1 ms. The value of k_1 calculated in this work corresponds to an intermediate species lifetime of 3 ms and probably determines the lifetime of the species in the micellar core.

To identify the intermediate species A_1 and A_3 from their spectra, it is useful to compare the results of the flash photolysis of **2** and its methylated analogue **3**, for which a single intermediate species (carbocation) is observed in water and methanol, its decay rate constant being close to that for **2**. However, unlike DHQ **1** and **2**, the formation of the aminyl radical for **3** was not observed. In hexane and isopropanol solutions of **3**, the formation of short-lived intermediate species was observed. The quantum yields of their formation were very low, and this did not allow us to investigate this process in detail. The photolysis of the micellar solutions of **3** in CTAB gives a carbocation with a decay rate constant close to that in water (table) and does not give any intermediate species decaying via a second-order reaction. However, two intermediate species with similar spectra are formed in comparatively high yields, and they are characterized by an absorption peak at λ_{max} = 470 nm (Fig. 2b, curve *1*). One of these decays with the rate constant k_1, and the other is practically sta-

Fig. 1. The decay curves of intermediate absorbance at λ_{reg} = 430 nm (*1*) and (*2*) and 450 nm (*3*) after pulse excitation with a light 300 nm < λ_{ex} < 400 nm of the CTAB micellar solutions of DHQ (*1*) **1**, (*2*) **2**, and (*3*) **3**; (a) and (b) points—experimental data, (*1*) and (*2*) solid line—approximation according to Eq. (2) and (*3*) solid line—approximation according to Eq. (3); (c) the gray line, experimental data and the black line, corresponding approximation. [DHQ] = 5×10^{-4} mol/l, [CTAB] = 0.01 mol/l, 22°C.

Decay rate constants of the intermediates generated in the photolysis of **1**–**3** in CTAB micellar solutions (k_1, k_2, $2k_3/\varepsilon$) and in water (k_w) at 22°C

Compound	k_1, s^{-1}	k_2, s^{-1}	$2k_3/\varepsilon$, cm/s (λ_{max}, nm)	k_w, s^{-1}
1	300	25 ± 1	480 ± 160 (430)	22 [7]
2	300	7.0 ± 0.3	100 ± 30 (450)	5 [7]
3	300	6.0 ± 0.3	80 ± 4 s^{-1}*	5.6

* First-order rate constant k_3 (Eq. (3)).

ble over 5 s. One more intermediate species, with a broad absorption band with λ_{max} = 450 nm (Fig. 2b, curve *2*), is also generated, whose first-order decay rate constant is 80 s^{-1} (Fig. 1, curve *3*). The yield of this intermediate decreases with a decrease in the CTAB concentration, and this is not observed at [CTAB] < 0.005 mol/l. The study of the nature of these intermediate species is in progress, but, by analogy with N-substituted dihydroquinolines with electron-accepting substituents in their aromatic ring and in the heterocycle [22] and with 1-acetyl-2,2,4-trimethyl-1,2-dihydroquinoline [23], the reversible cleavage of the N–C(2) bond of the heterocycle may occur in this case to yield several structural isomers.

These results allow the assumption that the intermediate species A_1 and A_3 for DHQ **1** and **2**, whose absorption spectra are similar, are the corresponding aminyl radicals. The rate constant k_1 probably characterizes the exit of the radicals from the micellar core, where they are generated, into the Stern layer and the aqueous phase, where they recombine with the rate constant k_3. The calculated value of the parameter $2k_3/\varepsilon_\lambda$ is 3–4 orders of magnitude lower than the corresponding values for hydrocarbon solutions [5, 10, 18]. Such a dramatic decrease in the rate constant of aminyl radical recombination in micellar solutions may be one of the causes of the increase in the stoichiometric factor of inhibition observed for ethoxyquin (**2**) [4].

The total absorbance observed for compounds **2** and **3** is substantially higher than that for **1** at the same DHQ and surfactant concentrations (Fig. 1). The global analysis of the experimental data shows that this increase is mainly due to the increase in the yield of the intermediate species A_1, A_3, and A_4. The carbocation yield has similar values for compounds **1** and **2** and a somewhat larger value for compound **3**. This is consistent with the increased carbocation quantum yield for N-methylated DHQ [7]. The increase in the yield of the aminyl radical for DHQ **2** is in agreement with the fact that the N–H bond is stronger in **1** than in **2** [24]. The comparatively low recombination rate constant of **2** (table) reflects the lower activity of aminyl radicals generated from **2** in this reaction [5].

Additional information necessary for the interpretation of the results was provided by the study of DHQ steady-state photolysis in the CTAB micellar solutions (Fig. 3). The formation of the product with a λ_{max} of

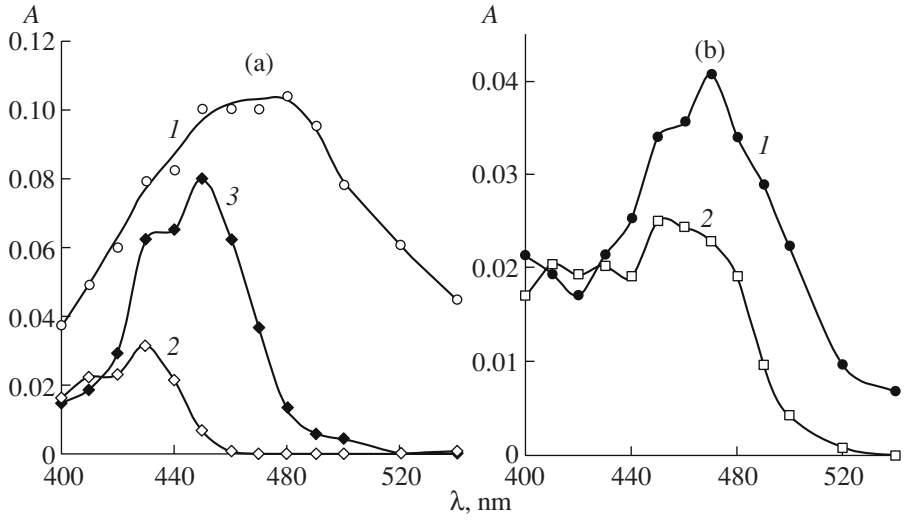


Fig. 2. The spectra of intermediate species calculated in the global kinetic analysis of experimental data of the flash photolysis of DHQ **1**–**3** in the CTAB micellar solutions: (a) (*1*) the carbocation spectrum (A2), (*2*) the spectrum of the aminyl radical of compound **1** (A1 and A3), (*3*) the spectrum of the aminyl radical of compound **2** (A1 and A3); (b) (*1*) the spectrum of intermediates A_1 and A_4 of compound **3**, and (*2*) the spectrum of intermediate A_3 of compound **3**.

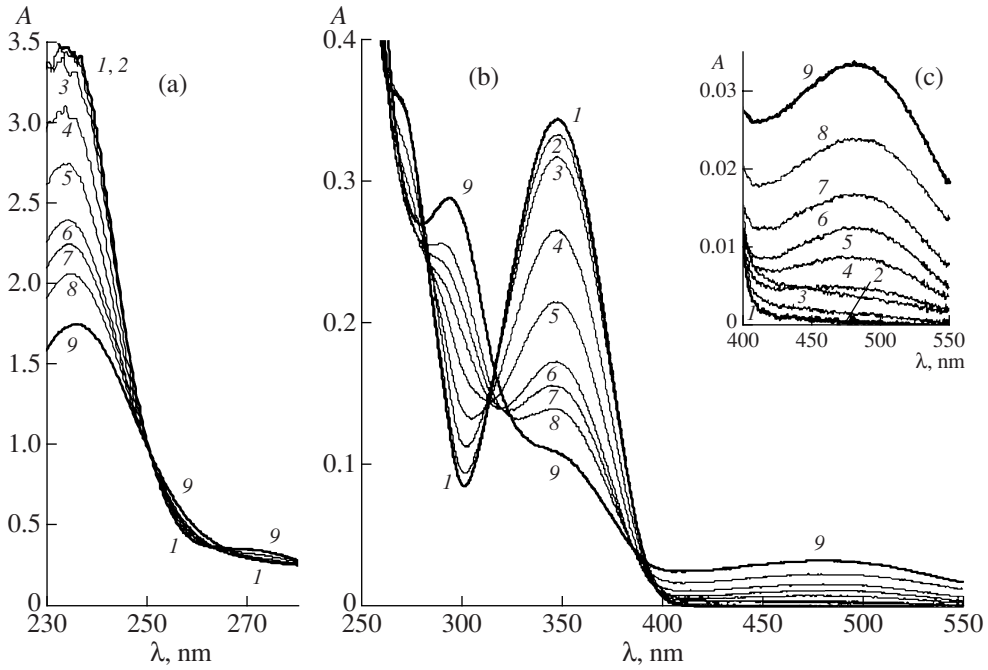


Fig. 3. The evolution of the absorption spectra of DHQ **1** in the course of steady-state photolysis in the CTAB micellar solution, time (min): (*1*) 0, (*2*) 2, (*3*) 5, (*4*) 12, (*5*) 20, (*6*) 35, (*7*) 45, (*8*) 60, and (*9*) 90; [DHQ] = 2×10^{-4} mol/l, [CTAB] = 0.0036 mol/l, 22°C.

~300 nm, which is typical of the products of water and methanol addition to DHQ, confirms the assumption that one of the intermediate species in the photolysis is a carbocation. However, the reaction in the micellar solution is more complex than that in homogeneous aqueous and methanol solutions. This is confirmed by the observation of the absorption of products other than the water adduct, including the DHQ dimer. The increase in the absorbance in the red spectral region (λ_{max} ~ 480 nm) after the first 10 min of photolysis (Fig. 3c) can be attributed to Br_2 formation and is caused by secondary photolysis reactions with the participation of radical products, including products resulting from dimer photolysis. The assumption about the formation of free Br_2 is supported by the increase of absorbance in this spectral range with an increase in the CTAB concentration in the case of compounds **1** and **2** and by the absence of absorption in this spectral range in the photolysis of **3**, when there are no radical products. The complexity of the process is confirmed by the absence of isosbestic points in the spectra in Fig. 3, which are observed in the DHQ photolysis in water, methanol [7, 8], and SDS micelles, when the corresponding adduct is the only photolysis product. As the CTAB concentration decreases, the rate of the steady-state photolysis increases, the water adduct is formed in higher concentrations, and the spectral changes in the course of photolysis become progressively similar to those observed in aqueous solutions and SDS micelles.

CONCLUSIONS

The photolysis of 1,2-dihydroquinolines in micellar solutions is a complex reaction determined by the surfactant nature, the location of the DHQ molecules in micelles, and their concentration in the aqueous and micellar phases. Photolysis in SDS micelles is similar to photolysis in aqueous solutions, with positive micellar catalysis being due to the fact that the DHQ molecules participate in proton abstraction from the intermediate cation and thus accelerate the reaction. In the CTAB micellar solutions, the intermediate species of a different nature are generated. These are carbocations and aminyl radicals, whose decay is described by different kinetic laws. The increase in the lifetime of the aminyl radicals generated from DHQ in micellar solutions may be one of the causes of the high effectiveness of ethoxyquin as an inhibitor of oxidation in micellar solutions.

ACKNOWLEDGMENTS

The author is grateful to E.N. Khodot (Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences), who kindly provided compound **3**.

This work was supported by the Department of Chemistry and Materials Science of the Russian Academy of Sciences through the programs "Theoretical and Experimental Study of Chemical Bonds and the Mechanisms of the Most Important Chemical Reactions and Processes" and "Biomolecular and Medicinal Chemistry."

REFERENCES

1. Nekipelova, T.D., *Izv. Akad. Nauk, Ser. Khim.*, 1994, no. 5, p. 948 [*Russ. Chem. Bull*. (Engl. Transl.), vol. 43, no. 5, p. 894].
2. Nekipelova, T.D., Pirogov, N.O., and Assovski, O.I., *J. Phys. Chem.*, 1995, vol. 99, no. 14, p. 4976.
3. Nekipelova, T.D. and Pirogov, N.O., *Izv. Akad. Nauk, Ser. Khim.*, 1997, no. 4, p. 708 [*Russ. Chem. Bull*. (Engl. Transl.), vol. 46, no. 4, p. 672].
4. Pryor, W.A., Strickland, T., and Church, D.F., *J. Am. Chem. Soc.*, 1988, vol. 110, no. 7, p. 2224.
5. Nekipelova, T.D., Malkin, Ya.N., and Kuzmin, V.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, no. 1, p. 80 [*Bull. Akad. Sci. USSR, Div. Chem. Sci.* (Engl. Transl.), vol. 29, no. 1, p. 67].
6. Nekipelova, T.D., Kurkovskaya, L.N., Levina, I.I., et al., *Izv. Akad. Nauk, Ser. Khim.*, 1999, no. 11, p. 2072 [*Russ. Chem. Bull*. (Engl. Transl.), vol. 48, no. 11, p. 2049].
7. Nekipelova, T.D., Shishkov, V.S., and Kuzmin, V.A., *Khim. Vys. Energ.*, 2002, vol. 36, no. 3, p. 212 [*High Energy Chem*. (Engl. Transl.), vol. 36, no. 3, p. 183].
8. Nekipelova, T.D., *Photochem. Photobiol. Sci.*, 2002, vol. 1, no. 3, p. 204.
9. Timr, L., Smelhausova, M., and Prusikova, M., *Angew. Macromol. Chem.*, 1993, vol. 206, no. 3, p. 199.
10. Gundstone, F.D., Mordi, R.C., Thorisson, S., et al., *J. Chem. Soc., Perkin Trans.*, 1991, no. 12, p. 1955.
11. Scaare, J.U. and Solheim, E., *Xenobiotica*, 1979, vol. 9, no. 11, p. 649.
12. Lockhart, B., Bonhomme, N., Roger, A., et al., *Eur. J. Pharmacol.*, 2001, vol. 416, no. 1, p. 59.
13. Berezin, I.V., Martinek, K., and Yatsimirskii, A.K., *Usp. Khim.*, 1973, vol. 42, no. 10, p. 1729 [*Russ. Chem. Rev.* (Engl. Transl.), vol. 42, no. 10, p. 1487].
14. Bunton, C.A., Nome, F., Quina, F.H., and Romsted, L.S., *Acc. Chem. Res.*, 1991, vol. 24, no. 12, p. 357.
15. Romsted, L.S., *J. Phys. Chem.*, 1985, vol. 89, no. 23, p. 5107.
16. Nekipelova, T.D., in *Chemical and Biological Kinetics: New Horizons*, Burlakova, E.B., Varfolomeev, S.D., and Zaikov, G.E., Eds., Leiden: Brill, 2005, vol. 1, p. 241.
17. Nekipelova, T.D., Levina, I.I., and Shishkov, V.S., *Kinet. Katal.*, 2004, vol. 45, no. 1, p. 28 [*Kinet. Catal.* (Engl. Transl.), vol. 45, no. 1, p. 24].
18. Malkin, J.N., Pirogov, N.O., and Kuzmin, V.A., *J. Photochem.*, 1984, vol. 26, no. 2, p. 193.
19. Nigam, S., Belletete, M., Sarpal, R.S., and Durocher, G., *J. Chem. Soc., Faraday Trans.*, 1995, vol. 91, no. 14, p. 2133.
20. McClelland, R.A., *Tetrahedron*, 1996, vol. 52, no. 20, p. 6823.
21. Bolt, J.D. and Turro, N.J., *J. Phys. Chem.*, 1981, vol. 85, no. 26, p. 4029.
22. Kolc, J. and Becker, R.S., *J. Chem. Soc., Perkin Trans. 2*, 1972, no. 1, p. 17.
23. Lukyanov, B.S., Lukyanova, M.B., and Volbushko, N.V., *Khim. Geterotsikl. Soedin.*, 2005, vol. 41, no. 7, p. 1103 [*Chem. Heterocycl. Compd.* (Engl. Transl.), vol. 41, no. 7, p. 936].
24. Kopytina, M.V. and Meleshina, A.M., *Zh. Prikl. Spectrosk.*, 1971, vol. 14, no. 6, p. 1063.