Effect of pH on kinetics of the decay of the radicals formed during photolysis of 2,2,4,6-tetramethyl-1,2-dihydroquinoline in aqueous and micellar solutions

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Kinetics of the decay of the transient radicals formed from 2,2,4,6-tetramethyl-1,2-dihydroquinoline (TMQ) in aqueous and micellar solutions of sodium dodecyl sulfate were studied by flash photolysis as a function of pH. In aqueous and micellar solutions of TMQ the mechanism of the decay of the transient species and the reaction products are different from those in homogeneous organic solutions. The decay of the transient radicals follows first-order kinetics in the entire range of pH under consideration in both aqueous and micellar solutions. In aqueous solutions at pH 9—12, the decay rate constant decreases from 25.3 to 3.7 s^{-1}. In micellar solutions at different pH, different types of micellar catalysis were observed. At pH 1, the rate constant in a micellar solution is slightly lower than that in an aqueous solution. At pH 3—11, the decay rate constant increases (positive micellar catalysis). The apparent rate constant depends linearly on the concentration of TMQ in micelles. The rate constant for the reaction of the transient radical cation with TMQ was determined (200 L mol^{-1} s^{-1}). At pH > 13, the decay rate constant in micelar solutions is lower than that in aqueous solutions (negative micellar catalysis).

Key words: flash photolysis, decay of radicals, micellar solutions, micellar catalysis, pH dependence.

The influence of organized media (micelles, vesicles, and membranes) on the course of a large variety of chemical reactions is now well documented.[1,2] On the one hand, modified reactivity of a "guest" molecule entrapped within or otherwise associated with a microphase is observed,[3] on the other, variation of the parameters of the chemical process is observed due to concentrating the reagents in a small volume.[1,4] These effects are particularly marked when ions take part in the reaction.[5] Of the ionic reactions studied most intensely, the reactions involving prototropic equilibria have received special attention, due to the unique features of micellar reaction media.[6]

In the last few years, our interests have been focused on the investigation of the behavior of hydroquinolines, which are well-known antioxidants for unsaturated compounds and biologically active substances, in micellar solutions.[7,8] The chemical and photochemical effects connected with the inclusion of hydroquinolines into micelles vary because the nitrogen atom of the parent compounds is protonated in moderately acidic solutions (pK_a 3—4), and the transient radicals are protonated in alkaline solutions (pK_a 9.5—13 depending on the substituents in the parent hydroquinoline).[9]

As a result of photolysis of 2,2,4,6-tetramethyl-1,2-dihydroquinoline (TMQ) in a neutral medium, we observed the generation of radical cations and neutral radicals, whose decay kinetics depended drastically on the nature of the medium (organic solvent, water, anionic (sodium dodecyl sulfate, SDS) or cationic (cetyltrimethylammonium bromide, CTAB) amphiphil). The formation of radical cations in water and in SDS micelles as a result of the photolysis of TMQ suggests that prototropic equilibria of both the parent TMQ and the transient radical should affect the rate of the reaction. In this context as a further extension of our studies, we report in this paper the pH dependence of the kinetics of the decay of transient radicals from TMQ in aqueous and SDS micellar solutions.

Experimental

2,2,4,6-Tetramethyl-1,2-dihydroquinoline (TMQ) was sublimed *in vacuo*. Sodium dodecyl sulfate (SDS) was recrystallized twice from ethanol. Bidistilled water was used. To prepare solutions with pH < 7, citrate buffer was used.[10] Solutions with pH 10.3, 11.3, and 13.3 were adjusted using NaOH (analytical grade, Chemapol). For solubilization, a weighted portion of TMQ in water or SDS solution was treated in an ultrasonic bath for 30 min at 40 °C and then stored at room temperature for 3 h.

Absorption spectra of the parent compounds and the final photolysis product were recorded on a Specord UV-VIS spec-

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trophotometer (Germany). Absorption spectra and decay kinetics of short-lived transient radicals were studied using a flash photolysis instrument with a resolution time of 5 μs that has been described in detail elsewhere.[11] Steady-state photolysis was carried out with a DRSh-1000 mercury lamp using a UFS-5 filter. All measurements were carried out at 24 °C.

Results and Discussion

In Fig. 1, the absorption spectra of the transient species generated by flash excitation of TMQ are presented. Previously,[12] it has been shown that in organic solvents the photolysis products are radicals formed as a result of homolytic dissociation of an N—H bond and a hydrogen atom; in acidic and polar media, the generation of radical cations is observed. In organic solvents, the absorption maximum of the neutral radicals is 410 nm, and that of the radical cation is 480 nm.

From Fig. 1 it follows that, depending on the pH of the medium, two types of transient species are also formed in water, with λ_{max} 410—420 nm and 460—490 nm, respectively. The spectra of the transient species in neutral aqueous and micellar solutions of SDS and CTAB have been assigned.[8] From the spectra given in Fig. 1, it follows that in acidic and neutral media only the radical cation is formed; in alkaline solutions, a neutral radical is generated, and when the pH is close to the value of pK_a of the radical, which is 10.3,[9] both types of radicals are recorded. In micellar solutions, the same products are formed (see Fig. 1, curve *6*). However, the range of pH in which the two types of the radicals are observed, is shifted in the alkaline direction. The phenomenon of enhancement of the apparent value of pK_a in micellar solutions of anionic surfactants is well-known and is rationalized in the theory of micellar catalysis in terms of a pseudophase model of ionic exchange[13,14] and an electrostatic model.[15]

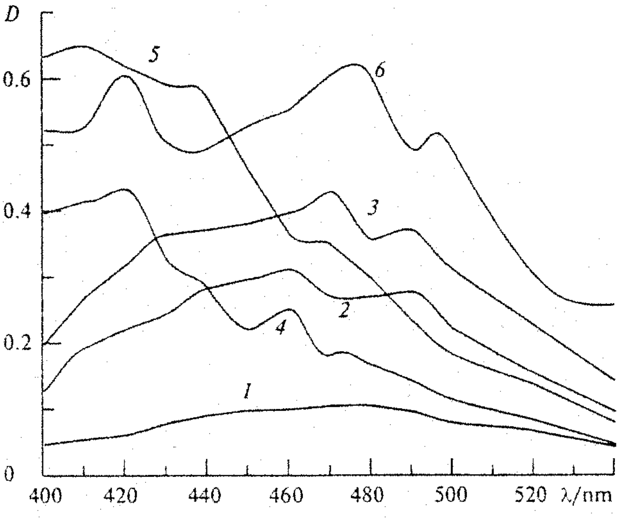

Fig. 1. Absorption spectra of the transient radicals generated upon flash photolysis of TMQ in aqueous solutions at pH 1 (*1*), 3.3 (*2*), 7 (*3*), 10.3 (*4*), 11.3 (*5*) and in the micellar solution of SDS at pH 11.3 (*6*).

In the micellar solution, the absorption maximum of the radical cation is shifted bathochromically by 10 nm from that in an aqueous solution. This shift may be the result of weakening of hydrogen bonding and a decrease in the polarity of the environment as a result of passing from water to micelles. This is often accompanied by an increase in the extinction coefficient.[6] In fact, we observed an increase in the absorption at the same flash energy when passing from aqueous to micellar solutions. The increase in absorption may be the result of the fact that concentrating the parent dihydroquinoline in the micelles increases the probability of its reaction with the hydrogen atom formed by the dissociation of the N—H bond (Scheme 1) (RNH is the parent dihydroquinoline and RN· is the radical formed from it).

Scheme 1

$$\mathrm{H + RNH \longrightarrow H_2 + RN^{\cdot}}$$

The higher the pH, the higher the increase in absorption of the transient species in the micellar solution. At pH 1, the increase in the intensity does not exceed 40% and depends on $[\mathrm{TMQ}]_0$. At pH 13.3, an almost twofold increase in the intensity of the band at λ 430 nm occurs independently of $[\mathrm{TMQ}]_0$. It is worth noting that the yield of the transient radicals increases with increasing pH at the same flash power (see Fig. 1).

As is known, the radicals generated from dihydroquinolines in organic solvents decay according to second-order reactions of head-to-head[12] or head-to-tail[16] dimerization. In polar solvents a disproportion-

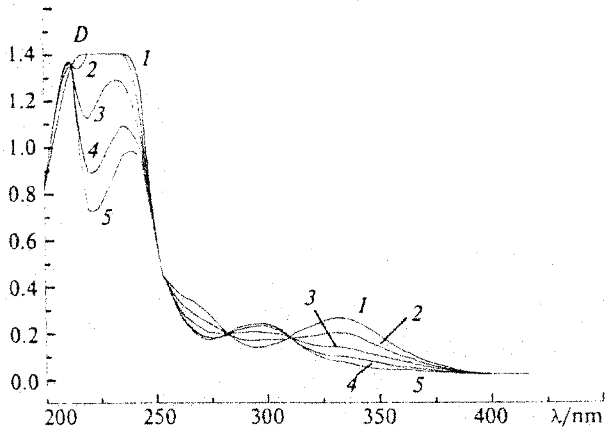

Fig. 2. Absorbance changes during the steady-state photolysis of TMQ in the aqueous solution, pH 7. The photolysis time, min: 0 (*1*), 2 (*2*), 5 (*3*), 10 (*4*), 15 (*5*).

ation reaction can occur yielding a compound with a quinoid structure and regenerating the parent dihydroquinoline.[17]

At all pH values the photolysis of TMQ under steady-state conditions yields only one product in both aqueous and micellar solutions. The spectrum of this compound in a neutral aqueous solution is presented in Fig. 2. The spectrum of the product formed in acidic solutions differs from that given in Fig. 2. However, after alkalization of the solution, it coincides with the spectrum given in Fig. 2, indicating the formation of the cationic form of the product in acidic media.

The spectra of the compound formed in aqueous and micellar solutions have an intense absorption band at λ_{max} 295 nm (in water). In the short-wave region in the spectrum of the product, instead of the single band at λ_{max} 225 nm found in the spectrum of TMQ, we recorded two bands at λ_{max} 207 and 250 nm (see Fig. 2). For comparison, the spectrum of the dimer product of the photolysis in organic solvents (heptane and 2-propanol) has the same absorption maxima as the parent compounds, only the extinction coefficients are different. The results of analysis of the products of the photolysis will be reported in subsequent papers, but the character of the absorption spectrum allows us to propose that the product formed has a quinoid structure (compare with the spectrum of 2,2,4-trimethyl-6-quinolone[17] formed during oxidation of ethoxyquin by Ag_2O in acetone[16]).

The change in the direction of the photolysis of TMQ in various solvents is the result of the change in the medium polarity and the formation of hydrogen bonds of different types. Passing from 2-propanol to water results in a hypsochromic shift of the absorption band of TMQ by 16 nm (λ_{max} 333 nm).[7] Similar shifts of absorption bands depending on the solvent have been observed for phenols.[18,19] It has been shown that, when a hydrogen bond forms, phenols can play the role of both a donor and acceptor of protons depending on the solvent. In the first case, there is a bathochromic shift of the absorption band compared to that in a solvent that does not form hydrogen bonds and, in the second case, a hypsochromic shift of the absorption band is observed. In alcohols, phenols are more often proton donors, and in water they usually are proton acceptors. The direction of the band shifts in the case of hydroquinolines is the same as that for phenols. This observation allows us to conclude that, on passing from 2-propanol to water, the nature of the hydrogen bond changes resulting in a change in the direction of the reaction of the transient radicals.

Unlike in organic solvents, the kinetics of the decay of transient species in aqueous and micellar solutions at any pH rigorously follow first-order reaction kinetics when $\lambda > 430$ nm ($r \geq 0.998$). The rate constants measured at different wavelengths coincide at the same pH. At pH 3—11.3, at the initial times ($t < 10$ ms), deviation from first order is observed for the kinetic curves monitored at $\lambda \leq 430$ nm (Fig. 3). In strongly acidic (pH 1) and alkaline (pH 13.3) solutions, *i.e.*, in solutions where the parent compound and the transient radical are in the same form (cationic or neutral), deviations from first-order kinetics are not observed in the entire range of wavelengths. It is obvious that at pH 3—11.3 a transient species that absorbs at $\lambda \leq$ 430 nm, decays with a higher rate constant, and can be a precursor of the radical cation is generated. This species does not form in a strongly acidic medium from the cationic form of the parent dihydroquinoline, which may be a reason for the low yield of the radical cation under these conditions.

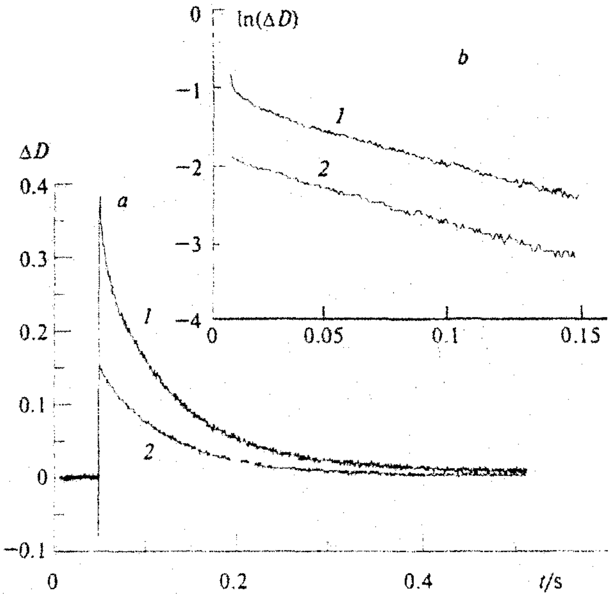

Fig. 3. Decay kinetic curves for the transient species generated upon flash photolysis of TMQ in water (*a*) and their presentation in semi-logarithmic coordinates (*b*). Registration wavelength, λ/nm: 420 (*1*), 470 (*2*); [TMQ] $1.65 \cdot 10^{-4}$ mol L^{-1}, pH 10.6.

As follows from the data given in Table 1 and Fig. 4, at pH < 8 the rate constant for the decay of transient radicals in water is practically constant and equal to ~25.3 s^{-1}. At pH 8—13, it drops to 3.7 s^{-1}. The apparent rate constant at a given pH does not depend on the concentration of TMQ and is the same for the radical and the radical cation.

The results obtained can be described assuming that the rate-determining step of the transformation of the transient radical to the reaction product is a first-order or pseudo-first order reaction, and the rate constants for this transformation are different for a radical and a radical cation. Thus, the simplest scheme of this transformation taking into account the acid—base equilibrium is as follows (Scheme 2) (P is the reaction product).

Scheme 2

$$\mathrm{RNH}^{+\cdot} \xrightarrow{k_1} \mathrm{P}$$

$$\mathrm{RN}^{\cdot} \xrightarrow{k_2} \mathrm{P}$$

$$\mathrm{RNH}^{+\cdot} \overset{K_a}{\rightleftharpoons} \mathrm{RN}^{\cdot} + \mathrm{H}^{+}$$

In this case, the apparent first-order rate constant is equal to

$$k_{\mathrm{app}} = \frac{k_1[\mathrm{H}^+] + K_a k_2}{[\mathrm{H}^+] + K_a}. \qquad (1)$$

In Fig. 4, the pH dependence of k_{app} calculated by Eq. (1) is plotted for $k_1 = 25.3\ \mathrm{s}^{-1}$, $k_2 = 3.7\ \mathrm{s}^{-1}$, and $K_a = 5 \cdot 10^{-11}$ mol L^{-1} (pK_a = 10.3)[9]. As can be seen in Fig. 4, Eq. (1) reflects the experimentally observed variations in k_{app} as a function of pH.

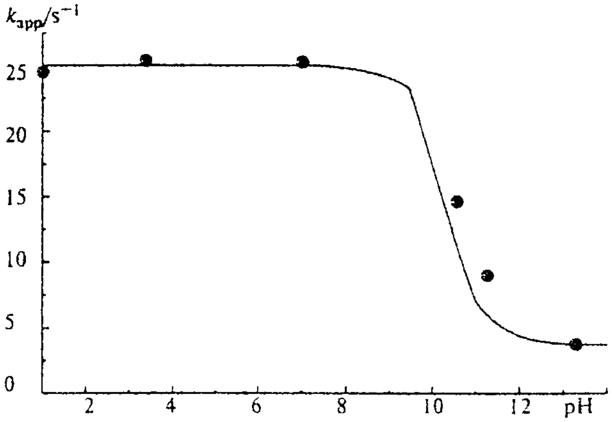

Fig. 4. k_{app} as a function of pH: points are the experimental values, the line is calculated by Eq. (1).

In Table 2 the rate constants obtained in this work for micellar solutions at various pH are listed as a function of the concentrations of TMQ and SDS. In contrast to the situation in aqueous solutions, the rate constant for the decay of transient species at given pH in micellar solutions does depend on the concentrations of TMQ and SDS. This dependence is different at various pH. For this compound, we observe different cases of micellar catalysis as a function of pH: at pH 1 and 13.3 there is typical negative catalysis (the apparent rate constant in the micellar solution is lower than that in the aqueous solution); at pH 7 and 11.3 there is positive micellar catalysis (the apparent rate constant is higher than that in water).

The apparent first-order rate constant in a micellar solution is defined by expression[1,4]

$$k_{\mathrm{app}} = \frac{k_{\mathrm{w}} + k_{\mathrm{m}}(P-1)CV}{1 + (P-1)CV}. \qquad (2)$$

where k_{w} is the rate constant in water, k_{m} is the rate constant in the micellar phase, P is the partition coefficient of a substance between aqueous and micellar phases, C = [SDS] − c.m.c., c.m.c. is the critical micellar concentration, and V is the molar volume of the surfactant. Negative micellar catalysis for a first-order reaction means that the rate constant in the micellar phase is lower than that in the aqueous phase, *i.e.*, $k_{\mathrm{w}} > k_{\mathrm{m}}$. From the experimental data it follows that (see Table 2) for the radical cation the decrease in the rate constant on passing from the aqueous to the micellar phase is small: $k_{\mathrm{w}} = 24.5\ \mathrm{s}^{-1}$, and the lowest measured value of $k_{\mathrm{app}} = 22\ \mathrm{s}^{-1}$. For the neutral radical, on passing from the aqueous to the micellar phase k_{app} is cut almost in half: $k_{\mathrm{w}} = 3.7\ \mathrm{s}^{-1}$, and the minimum $k_{\mathrm{app}} = 1.95\ \mathrm{s}^{-1}$. The decrease in the rate constant for radical decay in the micellar phase is connected with the fact that water plays a great role as a reagent in the process under study. The above-mentioned observation of the change in the direction of the reaction in aqueous media confirms this.

Table 1. Apparent first-order decay rate constant for the transient radicals (k_{app}) in water as a function of pH

pH	[TMQ]$_0 \cdot 10^4$ /mol L^{-1}	k_{app}/s^{-1}
1.0	9.20	24.9
1.0	6.13	24.0
1.0	3.07	24.6
3.3	3.00	24.9
3.3	1.50	26.0
7.0	2.30	25.4
7.0	1.26	24.9
10.6	3.30	15.2
10.6	1.65	13.5
11.3	Saturated	9.0
13.3	Saturated	3.7

Table 2. Apparent first-order decay rate constant for the transient radicals (k_{app}) in micellar solutions of SDS at various pH

pH	[SDS] $\cdot 10^2$ /mol L^{-1}	[TMQ]$_0 \cdot 10^4$ /mol L^{-1}	k_{app} /s^{-1}
1.0	8.00	9.6	23.1
1.0	8.00	4.8	22.3
1.0	8.00	3.2	21.8
1.0	4.00	3.2	21.8
7.0	7.90	10.5	46.0
7.0	7.90	2.1	29.0
7.0	3.95	2.1	25.9
11.3	7.97	4.7	34.1
11.3	5.30	4.7	37.9
11.3	2.66	4.7	60.0
13.3	8.30	5.4	1.97
13.3	6.92	5.4	1.95
13.3	5.54	5.4	2.23
13.3	4.15	5.4	2.42
13.3	2.77	5.4	2.72

Hence, the decrease in the concentration of water in the micellar phase may result in the decrease in the rate constant for the reaction.

At pH 7 and 11.3, the rate constant in the micellar solution is greater than that in the aqueous solution (compare Tables 1 and 2). The higher the concentration of TMQ at [SDS] = const and the lower the concentration of [SDS] at [TMQ] = const, *i.e.*, the higher the concentration of dihydroquinoline in the micelles, the higher the rate constant.

The dependence of k_{app} on the concentration of TMQ in the micelles indicates that there is a reaction between the radical cation and TMQ yielding the same reaction product. In water, this reaction does not manifest itself because of low concentrations of the reagents. In the micelles, the concentrations of TMQ and the radicals increase many times, and its role in the decay of the radicals becomes important.

We believe that this reaction occurs between the radical cation and the neutral parent molecule, because only when these species are in the solution at the same time do we observe an increase in k_{app} in the micellar solutions. At pH 1 and 13.3, when both compounds are either cations or in the neutral form, k_{app} is lower in the micelles than that in water. Hence, the reaction of the radical cation with the parent dihydroquinoline and the acid—base equilibrium for TMQ should be added to the kinetic scheme (Scheme 3).

Scheme 3

$$\mathrm{RNH}^{\cdot +} + \mathrm{RNH} \xrightarrow{k_4} \mathrm{P}$$

$$\mathrm{RNH_2}^{+} \rightleftharpoons \mathrm{RNH} + \mathrm{H}^{+}$$

To account for the concentration dependence of k_{app} in the micellar solution, we assumed[8] that decay of the transient species occurred as a result of recombination or disproportionation of the radical with the radical cation, and the rate-determining step of the reaction was formation of the neutral radical in the reaction of the radical cation with the parent dihydroquinoline. Computer simulation of the scheme suggested in Ref. 8 showed that, in fact, this made it possible to explain the regularities in the variation of k_{app} as a function of [TMQ] and [SDS] at pH 7, but only at this single value of pH. Expansion of this scheme to the regions with pH > 7 and pH < 7 did not lead to adequate reflection of the results observed.

The pseudophase model is usually employed to describe the kinetics of reactions in micellar solutions proceeding at rates that are lower than the exchange between micelles. Based on the pseudophase model, general approaches to the kinetic treatment of the reactions have been developed and successfully used for mono- and bimolecular reactions between neutral organic molecules.[4] Modification of the pseudophase model to simulate bimolecular ion—molecule reactions (the pseudophase model of ion exchange) has been described.[5,14] In this model, it is assumed that the reaction is pseudo-first order in the molecular component of the reaction, and the ionic component (usually a counterion) is in excess. In our case, at pH 3—11 a different situation occurs: we examine the kinetics of the decay of the ionic component (radical cation), and the neutral parent TMQ is in excess. For this case, we obtained adequate simulation of the observed results within the simple pseudophase model assuming that the concentrations of the radical cation and TMQ in micelles are determined by their partition coefficients P_1 and P_2, respectively. It is obvious that P_1 is determined by Coulomb and hydrophobic interactions, and P_2 is determined only by hydrophobic interactions.

The apparent rate constant for the decay of the radical cations depends on the rate constants for the reactions given in Schemes 2 and 3 (k_1 and k_4, respectively) and occurring in the aqueous and micellar phases. Assuming $(k_4)_m = (k_4)_w = k_4$ and expressing the concentrations of TMQ and the radical cation in the micellar and aqueous phases in terms of the total concentrations in the bulk solution, we obtain the following expression for the apparent rate constant in the micellar solution of SDS:

$$k_{app} - k_1 = k_4 \frac{[\mathrm{TMQ}]_0 P_1 P_2 CV}{(1 + CVP_1)(1 + CVP_2)}. \tag{3}$$

After transformation, Eq. (3) converts to:

$$\frac{[\mathrm{TMQ}]_0}{k_{app} - k_1} = \frac{1}{k_4 P_1 P_2 CV} + \frac{1}{k_4 P_1} + \frac{1}{k_4 P_2} + \frac{CV}{k_4}. \tag{4}$$

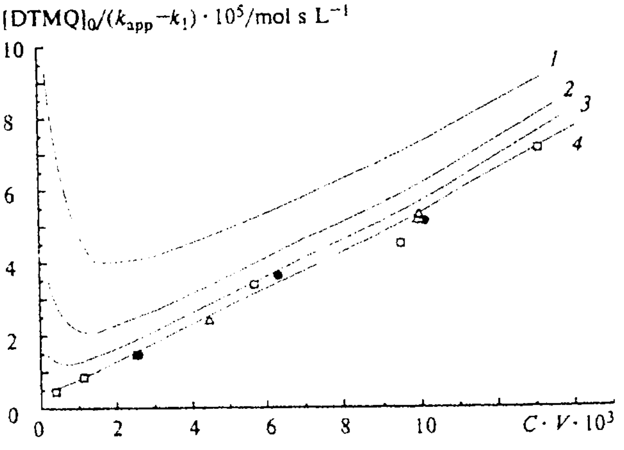

Fig. 5. Calculated dependences of k_{app} against the concentration of [TMQ] and [SDS] in the coordinates of Eq. (4) at k_4 = 200 L mol^{-1} s^{-1} and various values of *P*: 500 (*1*), 1000 (*2*), 1800 (*3*), 3700 (*4*). Points represent the experimental results obtained earlier[8] at pH 7 (□) and in this work at pH 7 (△) and 11.3 (•)

It is obvious that, when P_1 and P_2 are high enough, Eq. (4) may be reduced to the form:

$$\frac{[\mathrm{TMQ}]_0}{k_{\mathrm{app}} - k_1} = \frac{2}{k_4 P} + \frac{CV}{k_4}, \qquad (5)$$

where $P = 2P_1P_2/(P_1 + P_2)$, *i.e.*, the expression $[\mathrm{TMQ}]_0/(k_{\mathrm{app}} - k_1)$ should be a linear function of CV. In Fig. 5 the data obtained in Ref. 8 at pH 7 and in this work at pH 7 and 11.3 are presented. When plotting dependence (5), we used $V = 0.14$ L mol^{-1}, which corresponds to the molar volume of the Stern layer,[5] where, as shown earlier,[7] the molecules of dihydroquinolines are located. The results obtained at different pH lie in the same straight line. From the slope of the line, the rate constant $k_4 = (200\pm10)$ L mol^{-1} s^{-1} was determined. From the intercept, the mean distribution coefficient was estimated $P = (3700\pm1500)$.

In Fig. 5, we present also the dependences of $[\mathrm{TMQ}]_0/(k_{\mathrm{app}} - k_1)$ on CV calculated from Eq. (4) for $k_1 = 25.3$ s^{-1} and $k_4 = 200$ L mol^{-1} s^{-1} at various values of P. One can see that, when $P = 1000$, the linear dependence (5) is valid at $CV > 2 \cdot 10^{-3}$, when $P = 1800$ it is valid at $CV > 1 \cdot 10^{-3}$, and when $P = 3700$ it is valid at $CV > 2 \cdot 10^{-4}$, *i.e.*, in the entire range of the SDS concentrations used. As follows from Fig. 5, at the values of k_4 and P obtained experimentally, Eqs. (4) and (5) coincide at these concentrations. Computer simulation of the mechanism involving the reactions of Schemes 2 and 3, which occur in aqueous and micellar phases, and transfers of the reacting species between the phases completely coincide with the results obtained from Eq. (4) at pH 7 and 11.3. These computations agree qualitatively with the experimental observations at other pH.

Thus, we have shown that, in aqueous and micellar solutions, the mechanism of the decay of the transient radicals generated by the photolysis of TMQ is different from that in homogeneous organic solvents, resulting in the formation of different final products. It is doubtless that hydrogen bonding with water plays an important role in this transformation.

The decrease in the decay rate constant for the transient radical in water when the pH is close to the value of pK_a of the radical cation indicates unambiguously that conversion of the radical cation into the final product proceeds with a higher rate constant than that of the neutral radical. At pH 3—11, the formation of the reaction product in SDS micelles is accelerated because of the reaction of the radical cation with TMQ (positive micellar catalysis). The decrease in the rate constant in an alkaline solution (pH 13.3) indicates that the decay of the neutral radical occurs more slowly in micelles than in water, probably because of the decrease in the concentration of water and the change in the medium polarity.

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