Kinetics and Mechanism of the Photoinduced Addition of Water and Methanol to the Double Bond of 2,2,4-Trimethyl-8-Methoxy-1,2-Dihydroquinoline

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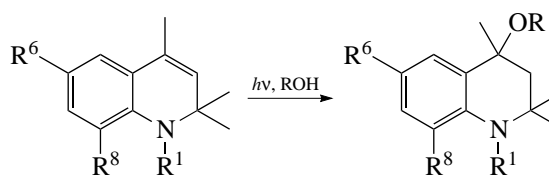
Abstract—The mechanism of the photoinduced Markovnikov addition of water and methanol to the double bond of 2,2,4-trimethyl-8-methoxy-1,2-dihydroquinoline was studied by flash photolysis over a wide range of acid and alkali concentrations. In neutral MeOH solutions, the successive formation of two active intermediates was observed. These intermediates have absorption bands at λ_{max} = 420 and 500 nm, respectively, and lifetimes of a few milliseconds. The rate constants of decay for these species (k_1 and k_2) were measured over the temperature range from 10 to 45°C, and the activation energies E_1 (3.7 ± 0.4) and E_2 (6.9 ± 0.7) kcal/mol were determined in MeOH. The addition of an acid accelerates the conversion of the former intermediate into the latter. The rate constant for the reaction of the former intermediate with the acid is $(2.0 \pm 0.4) \times 10^8$ l mol^{-1} s^{-1}. The latter intermediate was proposed to be a corresponding carbocation. In H_2O at pH < 9, the formation of the carbocation (λ_{max} = 500 nm) was observed on a millisecond timescale, with the lifetime being an order of magnitude higher than that in MeOH. In alkaline media, only the former intermediate (λ_{max} = 420 nm) was observed with a lifetime of 150 or 400 ms in MeOH or H_2O, respectively, at [NaOH] > 2×10^{-3} mol/l. The quantum yields of the product and the quantum yields of fluorescence were measured as functions of acidity. Possible mechanisms of the reaction are discussed.

INTRODUCTION

The Markovnikov addition of a solvent to olefins upon irradiation in water and methanol is one of the most documented organic photochemical reactions [1], which is not confined to acyclic alkenes. For various cyclic alkenes with $n \geq 6$, the mechanism discussed in the literature involves as a first step the photoisomerization of the starting *cis*-cycloolefin in the excited singlet state to the *trans* isomer upon direct irradiation [2–8]. The high degree of strain within the *trans*-cyclohexene structure represents a strong potential driving force for chemical reactions, which are not typical of the *cis* isomer [9, 10]. In methanol solutions, the highly strained *trans* isomer is protonated by the solvent to give the corresponding carbocation with the subsequent trapping of MeOH [6, 7]. Recently, we reported the results of identifying the products of the photolysis of 6- and 8-substituted 2,2,4-trimethyl-1,2-dihydroquinolines (DHQ) in water and methanol [11, 12]. The photolysis afforded quantitatively the Markovnikov adducts of the solvent, corresponding 6- and 8-substituted 4-hydroxy-
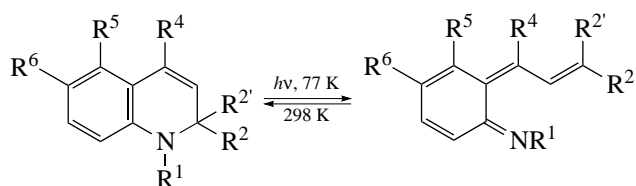
or 4-methoxy-2,2,4-trimerthyl-1,2,3,4-tetrahydroquinolines (Scheme 1):

R^6 = H, Me, OEt; R^8 = H, OMe; R^1 = H, Me; R = H, Me.

Scheme 1

The addition of EtOH and *n*-PrOH occurs only in the presence of water to afford a mixture of corresponding hydroxy and alkoxy adducts. Isopropanol does not give an adduct because of steric hindrance. In hydrocarbon solvents and dry alcohols with C > 1, the homolytic dissociation of the N–H bond occurs in secondary DHQ to give aminyl radicals [13, 14]. In pentane–ethanol–ether glasses at –196°C, N-substituted tertiary DHQ undergo the N–C(2) bond cleavage (Scheme 2) [15, 16].

Scheme 2

The photoinduced addition of H_2O and MeOH is insensitive to the presence of oxygen, and it most probably occurs from an excited singlet state [11, 12]. Nitrosubstituted DHQs do not undergo photoaddition, whereas DHQ with alkyl, alkoxy, and hydroxy substituents, as well as an N-methyl DHQ derivative, readily add water and methanol upon irradiation.

In this work, we examined the kinetics and mechanism of the photoinduced addition of water and methanol to 2,2,4-trimethyl-8-methoxy-1,2-dihydroquinoline in a wide range of acid and alkali concentrations by flash photolysis. The quantum yields of the overall reaction in acidic, neutral, and alkaline media were determined in steady-state experiments, and the quantum yields of fluorescence were measured.

EXPERIMENTAL

Materials. 2,2,4-Trimethyl-8-methoxy-1,2-dihydroquinoline (8-methoxy-DHQ) was synthesized by the condensation of *ortho*-anisidine with acetone [17]. The method was modified at the synthesis stage and especially at the stage of the isolation and purification of the desired compound. The reaction was carried out in a nitrogen atmosphere for 5 h. Acetone was added using a dosing tank at a rate that allowed keeping the temperature in the reaction flask within a range of 178–180°C and removing an acetone–water mixture by distillation within a temperature range of 65–75°C. The reaction mixture and the distillate were subjected to fractional distillation in vacuo with the subsequent recrystallization of the fractions 98–136°C (1 torr) and the bottoms from propanol-2 cooled down to 0–2°C. The precipitate was washed three times with cooled propanol-2 and dried in vacuo. An additional amount of 8-methoxy-DHQ was obtained upon the evaporation of the mother liquor and rectification of the residue over a zinc powder. The fraction with T_b = 120–135°C/(1 torr) was collected and recrystallized from propanol-2. Previously [17], 8-methoxy-DHQ was isolated as an oil with a yield of 30%. 8-Methoxy-DHQ synthesized in this study (52% yield on a reacted *ortho*-anisidine basis) was isolated as a white crystalline powder, mp 58–59°C. For $C_{13}H_{17}NO$, anal. calcd. (%): C, 76.81; H, 8.43; N, 6.89. Found (%): C, 76.96; H, 8.70; N, 6.78. ^1H NMR (DMSO-d_6), δ, ppm: 1.20 (s, 6H), 1.90 (s, 3H), 3.75 (s, 3H), 4.80 (s, 1H), 5.28 (s, 1H), 6.47 (t, J = 7.8 Hz, 1H), 6.68 (dd, J = 7.8 Hz, 1H), 6.72 (dd, J = 7.8 Hz, 1H). ^{13}C NMR (DMSO-d_6) (δ, ppm): 18.31, 30.69, 50.81, 55.30, 109.95, 114.56, 120.16, 127.38, 128.10, 132.89, 144.85. IR spectrum (KBr) (cm^{-1}): 3200, 3073–3000, 1624, 1608, 1588, 1368, 1240, 1176, 1068. Mass spectrum, m/z (I_{rel}, %): 203 (14)–M$^+$, 188 (100), 173 (57), 157 (5), 145 (10), 115 (6), 94 (10), 77 (16), 65 (15), 51 (10), 39 (20).

Methanol for spectroscopy (Merck) purified of water and acid traces by distillation over $Mg(CH_3O)_2$ and twice distilled water were used as solvents.

Flash photolysis. The absorption spectra and the kinetics of decay of transient species were examined on a flash photolysis instrument with a resolution time of 10 μs [18]. Samples were irradiated in a 10-cm quartz cell by a Xe lamp with a flash energy of 150 J. Absorbance changes were detected by a monitoring system consisting of a Xe lamp (75 W), a ZMP-3 monochromator, and a photomultiplier tube connected to an S9-8 digital storage oscilloscope (Russia). Digitized data were transferred to a Pentium 200 PC for data processing. In order to excite the long-wavelength band of 8-methoxy-DHQ (λ_{max} = 332 and 342 nm in H_2O and MeOH, respectively), the light was filtered through a UFS-5 filter (transmittance region of 300–400 nm with a maximum transmittance at 365 nm).

Quantum yields. The quantum yields of the consumption of 8-methoxy-DHQ and the formation of final tetrahydroquinoline were measured under continuous irradiation with light from a DRSh-1000 mercury lamp filtered with a UFS-5 filter. The absorbed light flux was measured by actinometry using the ferrioxalate actinometer [19]. The rates of disappearance of the initial DHQ and formation of the final product were determined from the absorption spectra in the UV–VIS range (Fig. 1) or from the fluorescence spectra of 8-methoxy-DHQ in alkaline solutions, because the measurements from the UV spectra are difficult to perform on account of the formation of by-products. These two methods gave consistent results in neutral and acidic solutions.

Corrected fluorescence spectra were measured with an Aminco Bowman spectrofluorimeter. Fluorescence quantum yields were measured using 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP) as a standard substance. The absorption and fluorescence bands of POPOP (λ_{max} = 345 nm and λ_{fl} = 430 nm) [20] are close to the corresponding bands of 8-methoxy-DHQ (λ_{fl} = 442 nm).

The absorption spectra in the UV–VIS region were measured with a Shimadzu UV-1601 PC spectrophotometer in quartz cells with an optical path length of 1 cm.

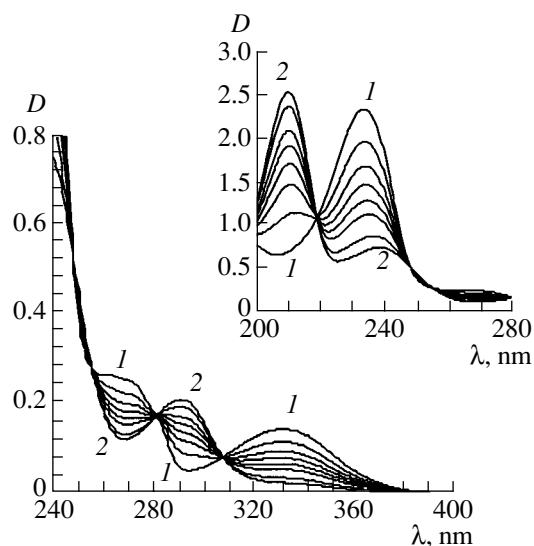**Data processing** was carried out on a Pentium 200 PC with the use of MS Excel (Solver).

Fig. 1. Evolution of the spectrum of 8-methoxy-DHQ during the steady-state photolysis in water: (*1*) parent 8-methoxy-DHQ and (*2*) final 4-hydroxy-8-methoxy-THQ. $T = 20°C$. The times of spectrum registration, min: 0, 2, 4, 6, 8, 10, 15, and 20.
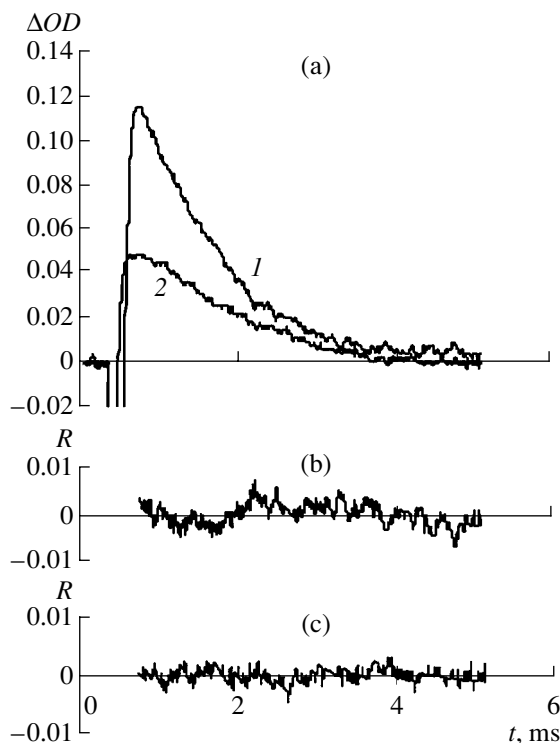

Fig. 2. (a) Kinetic curves of formation and decay of intermediate species monitored after the flash irradiation of 8-methoxy-DHQ in MeOH at (*1*) 440 and (*2*) 500 nm; $T = 20°C$. Residuals (*R*) obtained after the processing of experimental data according to Eq. (1) for curves (b) *1* and (c) *2*.

RESULTS AND DISCUSSION

Photolysis of 2,2,4-Trimethyl-8-Methoxy-1,2-Dihydroquinoline in Methanol

The typical kinetic curves observed in the flash photolysis of 8-methoxy-DHQ at various wavelengths are given in Fig. 2a. The initial absorbance and the amounts of the final product increase linearly with increasing intensity of the flash, indicating a monophotonic character of the reaction. Both the absorption spectra of the transient species and the observed rate constants are unchanged on going from deaerated to oxygen-saturated solutions. As a result of flash photolysis, the adduct of methanol to the double bond of the heterocycle is formed quantitatively, as in steady-state photolysis.

As follows from Fig. 2a, the kinetic curves observed in MeOH have a complex shape. The decay of absorbance in the initial portions of the curves observed at $\lambda_{mon} < 460$ nm (curve *1*) is slower than that in the second portion of the kinetic curve described by an exponential law. The higher the registration wavelength, the slower the decay. At $\lambda_{mon} > 460$ nm (curve *2*), the formation of the product is observed at the initial portion of the curve, which is followed by a decay. At temperatures higher than 20°C, the deviation from an exponential law decreases, thought remains reliably distinguishable. The experimental kinetic curves were adequately approximated on the assumption that the reaction proceeds in two consecutive steps ($\mathbf{A} \longrightarrow \mathbf{B} \longrightarrow \mathbf{C}$, where $\mathbf{A}$ and $\mathbf{B}$ are transient species, and $\mathbf{C}$ is

the product). The following equation describes the kinetic curves of this reaction sequence:

$$\Delta OD = A_1 \exp(-k_1 t) - A_2 \exp(-k_2 t), \quad (1)$$

where ΔOD is the experimental change in the absorbance; $A_1 = \varepsilon_A[\mathbf{A}]_0 + \varepsilon_B[\mathbf{A}]_0 k_1/(k_2 - k_1)$, $A_2 = \varepsilon_B[\mathbf{A}]_0 k_1/(k_2 - k_1)$, k_1, and k_2 are the rate constants of the first and second steps, respectively; and ε is the molar absorption coefficient. The simultaneous processing of the whole array of the kinetic curves monitored at wavelengths from 400 to 600 nm using Eq. (1) gives the rate constants k_1 and k_2 listed in Table 1. The activation energies of these reactions are also given in Table 1. The rate constants of both reactions are approximately four to five times higher than those determined for 2,2,4,6-tetramethyl-1,2-dihydroquinoline (6-methyl-DHQ) [21]. It is worth noting that, unlike 6-methyl-DHQ, for which the activation energy of the first reaction is close to zero within the experimental error [21], E_1 for 8-methoxy-DHQ is equal to 3.7 ± 0.4 kcal/mol (Table 1). The activation energies of the second step for 8-methoxy- and 6-methyl-DHQ are similar and equal to 6.9 ± 0.7 (Table 1) and 7.5 ± 0.7 kcal/mol [21], respectively.

The spectra of transient species $\mathbf{A}$ and $\mathbf{B}$ were calculated from the parameters A_1 and A_2. The parameter A_2 is proportional to ε_B; that is, its values at different wave-
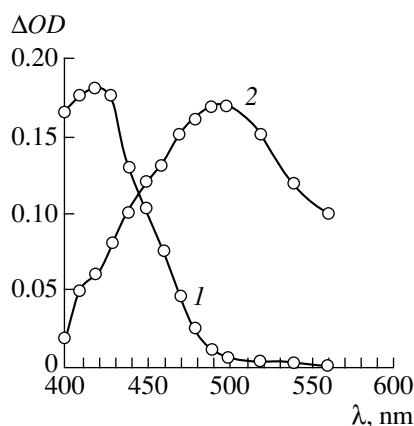
Fig. 3. Spectra of transient species (*1*) **A** and (*2*) **B** calculated from the kinetic curves of the flash photolysis of 8-methoxy-DHQ in MeOH at 20°C.

lengths represent the spectrum of **B**. The spectrum of **A** can be calculated as $A_1 - A_2$. The spectra thus obtained (Fig. 3) have absorption maximums at 420 and 500 nm for transient species **A** and **B**, respectively. Note that the initial spectrum monitored immediately after flash excitation is similar to the calculated spectrum for **A**.

In the methanol solutions of 8-methoxy-DHQ acidified with acetic acid at [AcOH] > 7×10^{-6} mol/l, the transient species **B** is observed immediately after flash excitation. These transients decay in a first-order reaction with a rate constant equal to k_2 calculated from Eq. (1) in neutral solutions (see Table 1). The transient **A** is quenched by AcOH with a rate constant of $(2.0 \pm 0.4) \times 10^8$ l mol^{-1} s^{-1}, which was calculated from a growth in the rate of the decay of **A** and the formation of **B** at the initial portion of the kinetic curve in the presence of the acid.

In alkaline methanol solutions, the transient species **A** (λ_{max} = 420 nm) was generated, and it decayed in a first-order reaction with the rate constant k_1^{app}, which decreased with alkali concentration (Fig. 4a). At [NaOH] > 10^{-3} mol/l, the lifetime of **A** attains 150 ms, that is, two orders of magnitude longer than the lifetime of this transient in the neutral solution (Table 1). In comparison with k_1 in neutral MeOH, the limiting rate constant of decay of the transient species **A** in alkaline solutions has a higher activation energy (7.8 ± 0.8 kcal/mol). It is clear that the limiting value of the rate constant k_1^{app} cannot be assigned to the thermal unimolecular conversion of **A** into initial DHQ because the calculated preexponential factor is 5.3×10^6 s^{-1}.

As mentioned above, the conversion of 8-methoxy-DHQ into 2,2,4-trimethyl-4,8-dimethoxy-1,2,3,4-tetrahydroquinoline (4,8-dimethoxy-THQ) is quantitative. This is clear from the occurrence of isosbestic points in the electronic spectra measured in the course of the reaction. The quantum yields of 8-methoxy-DHQ consumption and adduct formation are 0.22 in neutral solutions, and they do not change with the addition of AcOH (Table 2). In alkaline media up to [NaOH] = 10^{-4} mol/l, the quantum yield of the reaction does not vary in spite of a decrease in the value of k_1^{app} by almost an order of magnitude (cf. Figs. 4a and 4b). A further increase in the alkali concentration results in a drastic drop in the quantum yield of the reaction. The isosbestic points in the spectra disappear gradually, thus indicating the formation of by-products, although 4,8-dimethoxy-THQ remains the major product of the photolysis up to the concentration [NaOH] = 0.1 mol/l.

Table 1. Kinetic parameters of the reactions of transient species generated in the photolysis of 2,2,4-trimethyl-8-methoxy-1,2-dihydroquinoline in water and methanol at different acidities (the rate constants are given at 20°C)

Solvent	k_1, s^{-1}	k_2, s^{-1}	k_{-1}, l mol^{-1} s^{-1}	E_1, kcal/mol	E_2, kcal/mol
H$_2$O	>1000	65 ± 3	–	–	11.7 ± 1.2
H$_2$O + HCl	–	65 ± 3	–	–	–
H$_2$O + NaOH	2.5 ± 0.2*	–	–	13.5 ± 1.4	–
MeOH	900 ± 90	1830 ± 180	–	3.7 ± 0.4	6.9 ± 0.7
MeOH + AcOH	$(2.5 \pm 0.3) \times 10^8$**	1830 ± 90	$(4.5 \pm 1.0) \times 10^8$		6.9 ± 0.7
MeOH + NaOH	6.6 ± 0.7*	–	–	7.8 ± 0.8	–

  * At [NaOH] = 0.05 mol/l.

** Bimolecular rate constant for the reaction of intermediate **A** with an acid, l mol^{-1} s^{-1}.
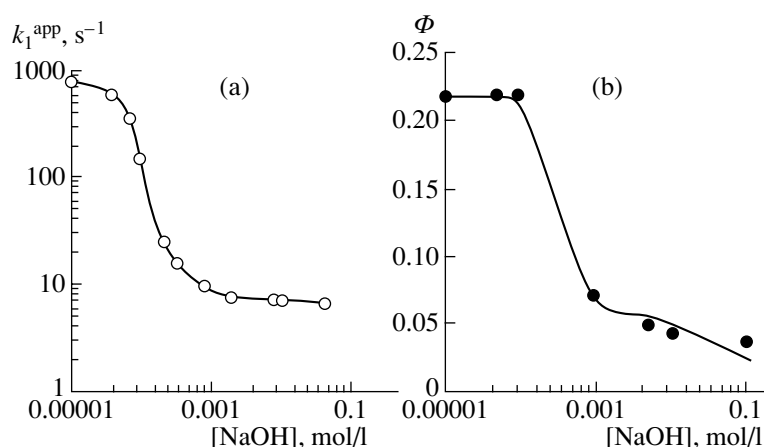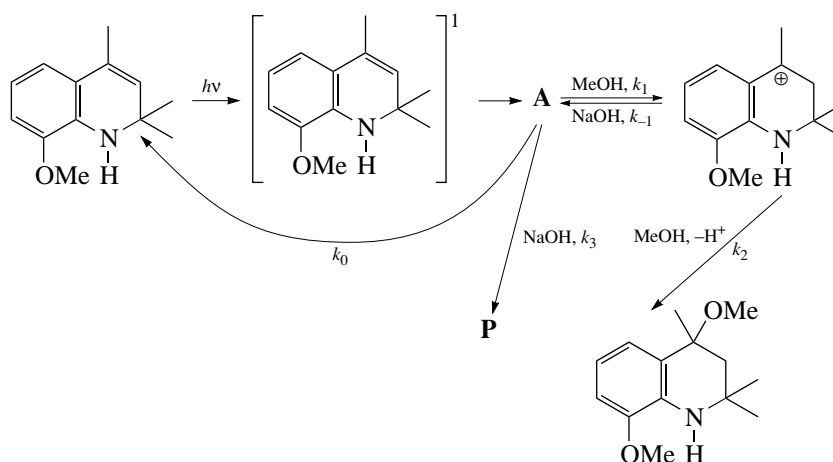
Fig. 4. (a) Rate constant of the decay of **A** (k_1^{app}) as a function of [NaOH] measured after the flash irradiation of 8-methoxy-DHQ in MeOH; $T = 20°C$. The points represent the experimental values, and the solid line at [NaOH] $> 10^{-4}$ mol/l is the fitting curve calculated according to Eq. (2) at $k_0 = 5.5$ s^{-1}, $k_{-1} = 4.5 \times 10^8$ l mol^{-1} s^{-1}, and $k_3 = 28$ l mol^{-1} s^{-1}. (b) The quantum yield of consumption of 8-methoxy-DHQ as a function of [NaOH] in the steady-state photolysis of 8-methoxy-DHQ; $T = 20°C$. The points represent the experimental values, and the solid line is the fitting curve calculated according to Eq. (3) at $k_0 = 5.5$ s^{-1} and the experimental values of k_1^{app}.

The photochemical reactions that occur upon the excitation of 8-methoxy-DHQ over a wide range of acid and alkali concentrations are summarized in Scheme 3. In fact, the experimental results obtained in neutral and acidic media strongly indicate that **B** is a cationic species. Since the addition occurs according to the Markovnikov rule, this should be a corresponding carbocation. The reaction of DHQ is the first example

of the photoinduced Markovnikov addition, when the successive formation of two intermediate species was observed. For the reaction of phenylcyclohexene (PCH), the kinetics of which was studied most thoroughly in solutions with various acid concentrations [5, 6], *trans*-cyclohexene was observed in neutral solutions and the corresponding carbocation was observed in acidic solutions.

Scheme 3

The concentration dependence of k_1^{app} can be rationalized in terms of the reversible conversion of **A** into **B** in an alkaline medium. The carbocation **B** can interact with NaOH to give either **A** or initial 8-methoxy-DHQ. The latter reaction cannot be ruled out com-

pletely; however, the substantial increase in the lifetime of **A** in alkaline media and the independence of the quantum yield of the product up to an alkali concentration of 10^{-4} mol/l with a decrease in k_1^{app} by an order of magnitude are consistent with the preferable formation
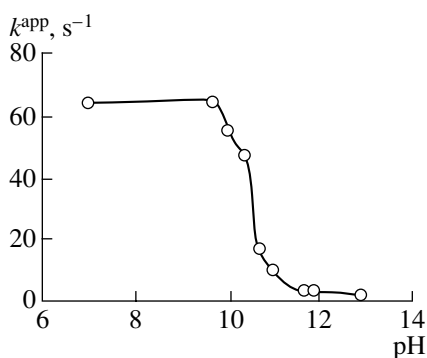
k^{app}, s^{-1}

Fig. 5. Apparent rate constant of the decay of transient species **A** and **B** in the photolysis of 8-methoxy-DHQ (k^{app}) in water as a function of pH; $T = 20°C$.

of **A** in this reaction. On the assumption that the concentration of **B** is quasi-stationary in alkaline media, the following equation can be derived for the apparent rate constant of the decay of **A**:

$$k_1^{app} = k_1 k_2 (k_{-1}[NaOH] + k_2)^{-1} + k_0 + k_3[NaOH], \quad (2)$$

where k_0 characterizes the thermal conversion of **A** into the initial DHQ and k_3 characterizes the formation of by-products in alkaline media with the participation of an alkali. On the assumption that k_1 and k_2 are equal to the experimental values obtained in neutral solutions, Eq. (2) adequately approximates the experimental curve in Fig. 4a at $[NaOH] > 10^{-4}$ mol/l and the rate constants $k_0 = 5.5 \times 0.5$ s^{-1}, $k_{-1} = (4.5 \pm 1.0) \times 10^8$ l mol^{-1} s^{-1}, and $k_3 = 28 \pm 10$ l mol^{-1} s^{-1}.

The suggested scheme allows us to explain the observed dependence of the quantum yield of 8-methoxy-DHQ consumption on the acidity. Indeed, in acidic and neutral media in the absence of side reactions when k_0 is low in comparison with k_1, the generated transient **A** is completely converted into the final product, the measured quantum yield is equal to the quantum yield of the formation of **A**, and the yield of the product should be quantitative. Therefore, the increase in the rate constant of the conversion of **A** into **B** in the presence of an acid does not affect the quantum yield of the reaction. In alkaline media, the product yield must only

Table 2. Quantum yields of 2,2,4-trimethyl-8-methoxy-1,2-dihydroquinoline consumption (Φ) and the quantum yields of fluorescence (ϕ_{fl}) in various solvents

Solvent	Φ	ϕ_{fl}
Heptane	0.016	0.23
i-PrOH	0.015	0.36
MeOH	0.22	0.06
MeOH + AcOH*	0.21	0.055
MeOH + NaOH*	0.037	0.06

* At [NaOH] or [AcOH] = 0.05 mol/l.

decrease due to the formation of by-products with the rate constant k_3 (Scheme 3). This was observed experimentally at high concentrations of NaOH. The quantum yield of 8-methoxy-DHQ consumption, when the lifetime of **A** increases due to the reversibility of reaction 1, should decrease due to the formation of the parent compound in the thermal reaction with the rate constant k_0 according to the equation

$$\Phi = \Phi_{MeOH}(k_1^{app} - k_0)/k_1^{app}, \quad (3)$$

where Φ_{MeOH} is the quantum yield of **A** in neutral media. The approximation of the experimental data given in Fig. 4b by Eq. (3) with the use of the experimental values of k_1^{app} gives $k_0 = 5.5 \pm 1.0$ s^{-1} (Fig. 4b). Thus, the values of k_0 calculated from independent experimental data on the dependence of k_1^{app} and the reaction quantum yield on [NaOH] coincide. As for the quantum yield of the product, it should be even lower due to the formation of by-products (see Scheme 3):

$$\Phi = \Phi_{MeOH}(k_1^{app} - k_0 - k_3[NaOH])/k_1^{app}. \quad (4)$$

Unfortunately, the experimental quantitative checking of Eq. (4) is difficult, because it is impossible to exactly determine the concentration of the product from the UV spectra under these conditions. However, as mentioned above, a decrease in the yield of the adduct due to the formation of by-products was observed qualitatively.

Photolysis of 2,2,4-Trimethyl-8-Methoxy-1,2-Dihydroquinoline in Water

Similarly to methanol, the direct photolysis of 8-methoxy-DHQ in water affords quantitatively 4-hydroxy-2,2,4-trimethyl-8-methoxy-1,2,3,4-tetrahydroquinoline (4-hydroxy-8-methoxy-THQ), the adduct of the solvent to the double bond according to the Markovnikov rule [12] (Fig. 1). However, the reaction kinetics changes. At pH < 9 immediately after flash excitation, the formation of a transient species with a maximum at 500 nm is observed. The generated transient species decays in the first-order reaction with a rate constant equal to 65 s^{-1}. With increasing pH, the spectrum of the transient species changes, and the observed rate constant decreases (Fig. 5). At pH > 11, a transient species with a maximum at 420 nm is generated, and it decays according to a first-order rate equation. By analogy with MeOH solutions, we assume that, in acidic, neutral, and weakly alkaline solutions, the formation of carbocation **B** is observed, and the transient species **A** is formed in alkaline solutions. The lifetimes of transient species in water are relatively high and vary from 15 ms for the carbocation in neutral and acidic media to 400 ms in alkaline solutions for transient **A**. Thus, the lifetime of the carbocation in water is more than an order of magnitude higher than that in

MeOH; this fact is consistent with the higher nucleophilicity of MeOH in comparison to water. As in the photolysis of 6-methyl-DHQ, the activation energy E_2 in water is higher than that in MeOH (see Table 1), and it is close to the value obtained for 6-methyl-DHQ [21]. In alkaline media at pH 11 and 13, the activation energies E_1 for k_1^{app} obs are close to one another within the limits of experimental error, although the rate constants at these pH values differ by more than three times.

Interestingly, the dependence of k_1^{app} on [NaOH] in aqueous solutions obeys the same regularities as in methanol. At [NaOH] $> 2 \times 10^{-4}$ mol/l, the dependence of k_1^{app} on [NaOH] fits well to Eq. (2) at the following values: k_1/k_{-1}: $k_1/k_{-1} \approx (1.0 \pm 0.2) \times 10^{-4}$ mol/l, $k_2 = 65$ s^{-1}, $k_0 = 2.1 \pm 0.5$ s^{-1}, and $k_3 = 3.8 \pm 1.0$ l mol^{-1} s^{-1}. Unfortunately, it is impossible to independently determine the value of k_1 in this case. However, if we assume that k_{-1} has similar values in water and MeOH, the value of k_1 is about 10^4 s^{-1}, that is, substantially higher than k_2. Because of this, we do not observe the formation of **A** in neutral solutions on the timescale that is used to observe the carbocation **B**.

The decrease in k_2 in H$_2$O in comparison with MeOH results in the fact that side reactions play a substantially greater role in aqueous alkaline solutions than in methanol alkaline solutions. In this case, the disappearance of isosbestic points from the spectra in the course of the steady-state photolysis is observed already at [NaOH] $> 10^{-4}$ mol/l. When the alkali concentration increases further, the character of the spectra changes drastically, the rate of 8-methoxy-DHQ consumption measured from the fluorescence spectra decreases by more than an order of magnitude, and the Markovnikov adduct is no longer the major product (cf. Figs. 1 and 6). Spectrum 2 (Fig. 6) was recorded after 1 h of photolysis. According to the fluorimetric data, 60% of the starting 8-methoxy-DHQ is consumed by this time. Along with a substantial change in the absorption spectrum of photolysis products in the UV region, a weak, but reliably detected, band in the visible region of the spectrum with a maximum at $\lambda = 540$ nm appears (Fig. 6, inset). Note that the quantum yields of fluorescence and the yield of intermediate **A** in the flash photolysis experiments do not depend on the alkali concentration in both MeOH and H$_2$O (Table 2).

Mechanism of the Photoaddition of Water and Methanol to 2,2,4-Trimethyl-8-Methoxy-1,2-Dihydroquinoline

As shown earlier [13, 14], DHQs dissolved in hydrocarbon solvents and dry alcohols with C > 1 undergo a homolytic scission of the N–H bond to afford aminyl radicals, which decay in a second-order reaction. The direction of the reaction changes crucially on going from water to methanol. In these solvents, the adduct of the solvent to the DHQ double bond is formed
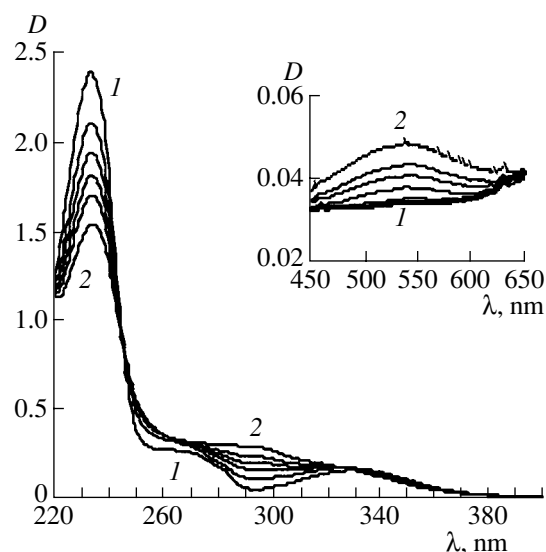

Fig. 6. Evolution of the spectrum of 8-methoxy-DHQ during the steady-state photolysis in water at [NaOH] = 0.1 mol/l: (*1*) parent 8-methoxy-DHQ and (*2*) after 60 min of photolysis. The times of spectrum registration, min: 0, 10, 20, 30, 45, and 60.

quantitatively. A comparison of the quantum yields of the two processes for 8-methoxy-DHQ (Table 2) demonstrates that the efficiency of the photoaddition is an order of magnitude higher than that of the homolytic cleavage of the N–H bond. Simultaneously, the quantum yield of fluorescence decreases by an order of magnitude, which also indicates an important role of the excited singlet state in the reaction. These results are consistent with the generally accepted view that, upon direct photolysis, the photoaddition to cyclohexenes [3–6] and dihydronaphthalenes [22, 23] occurs via an excited singlet state.

The key question concerns the nature of transient species **A** and **B** observed in the flash photolysis experiments. The experimental data given above indicate that transient **B** is the corresponding carbocation. By the example of 6-methyl-DHQ, it was shown [21] that the kinetic isotope effect of the formation of the carbocation in MeOH is 2.0, which is typical of proton transfer via the A-S_E2 mechanism [24].

The interpretation of the structure of **A** is more complex. The assumption that, like cyclohexenes, this intermediate is a strained *trans* isomer formed as a result of the *cis–trans* photoisomerization of initial 8-methoxy-DHQ raises many objections. The most important of these arises from the very long lifetimes of this species, which can be as long as 400 ms in aqueous alkaline solutions. It is clear that, in the case of DHQ, the *trans* configuration of the heterocycle should be more strained and, therefore, less stable than that for *trans*-PCH, which has a lifetime of 9 µs [5].

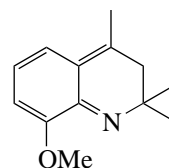DHQs are closer in structure to 1,2-dihydronaphthalenes (DHN) than to cyclohexenes. It was found that

3-methyl-DHN also adds MeOH in acidic media [23]. However, the structure of the carbocation precursor suggested in this case is impossible for DHQ. In the reaction of 4-methyl-DHN, which is closer in structure, the ether is a by-product, and the mechanism of its formation was not discussed in the literature [22, 23]. All assumptions on the mechanism of photoreactions of DHN were based only on the analysis of the products formed in steady-state experiments and were not confirmed by kinetic data. There are no published data on the spectra of transient species.

Thirty years ago, J. Kolc and R.S. Becker published the results on the formation of colored products upon the photolysis of several N-substituted DHQs in pentane–ethanol–ether glasses at –196°C [15, 16]. Upon heating up to ambient temperature, the coloration bleached to give parent DHQ. These results were interpreted in terms of N–C(2) bond scission (Scheme 2). The formation of *N*-cyano-*o*-aminocinnamaldehyde in the case of *N*-cyano-2-hydroxy-1,2-dihydroquinoline was strong evidence in favor of this assumption [16]. The colored intermediates considered in [15, 16] exhibit a broad band in the visible region with a maximum at 460–490 nm. The transient species generated from DHQ in water and MeOH have absorption bands in the same spectral region. However, our kinetic data are inconsistent with the assumption that **A** is an open *ortho*-quinoid structure. The long lifetime of **A** in alkaline solutions can be attained only in the case of the reversibility of reaction 1 (Scheme 3) or on the assumption that, under these conditions, **A** does not react with MeOH and H_2O, which is not the case. It is also difficult to imagine that the carbocation **B** gives an open *ortho*-quinoid structure in the reaction with NaOH.
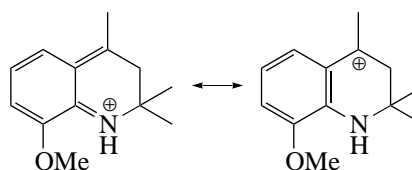
Recently, it was found [21] that *N*-methyl-6-methyl-DHQ gives a carbocation immediately after flash excitation on the nanosecond timescale. The addition of an alkali results in an acceleration of the decay of this species, and the formation of species **A** is not observed. Therefore, discussing either of the above mechanisms, one should bear in mind that transient **A** is only observed for secondary amines, that is, compounds with a hydrogen atom at the nitrogen atom of the heterocycle. As mentioned above, the reaction under study proceeds only in H_2O, MeOH, or higher alcohols in the presence of H_2O. The analysis of the UV spectra of 8-methoxy-DHQ in various solvents shows that the long-wavelength absorption band is blue-shifted by 16, 7, 3, and 3 nm in H_2O, MeOH, EtOH, and PrOH, respectively, in comparison with the spectrum in heptane. Such a difference in the spectra cannot only be attributed to the change in the solvent polarity taking into account that, in aprotic polar solvents, this band is weakly red-shifted. This means that hydrogen bonding plays an important role in changing the direction of the reaction in the case of DHQ. For secondary DHQ, two types of hydrogen bonding between DHQ and H_2O or MeOH are possible: (1) between the hydrogen atom of the solvent and the lone electron pair of nitrogen or aromatic π electrons and (2) between the hydrogen atom of the amino group of DHQ and the lone electron pair of the oxygen atom of the solvent. Theoretical and experimental data for indole give preference to the hydrogen bond formation of the second type [25, 26].

Hence, the following route for the formation of **A** can be suggested: intramolecular hydrogen transfer in the excited state assisted by H_2O or MeOH molecules, which act as a bridge between the N–H group and the double bond, to give the cyclic *ortho*-quinomethane imine structure

This structure should be high-energetic, but the reverse conversion into the initial 8-methoxy-DHQ is hindered; this fact explains the long lifetime of **A**. The cation formed by protonation has two resonance structures, with the second (carbocationic) being more stable:

Within the framework of this mechanism, the reaction of the carbocation with alkali to give **A** becomes possible. Moreover, the high value of $pK_a = 10.4$ (see Fig. 5) for the carbocation in water can be explained. Recently, it has been predicted theoretically [27] and shown experimentally [28] that *para*-quinomethane imine systems are more basic ($pK_a = 8.5$) than quinone imine systems ($pK_a = 3.7$) due to the stabilization of a positive charge in the aromatic resonance structure. As shown above, this stabilization is also possible in the *ortho*-quinoid structure suggested for **A**. One should bear in mind that the tautomerization in the reaction under consideration occurs only in the excited state. We failed to find even traces of 3-D-substituted DHQ upon storage and heating of the parent DHQ in a CD_3OD solution for a week. If the tautomerization occurred in the ground state, this product should have accumulated. We believe that the experiments on the identification of **A** and theoretical calculations will allow us to make an ultimate choice between the possible structures of **A**.

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