Laser flash photolysis study of the decay kinetics of carbocations of 1,2,2,4-tetramethyl-1,2-dihydroquinoline in the porous glass in the presence of methanol

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The efficiency of formation and the decay kinetics of carbocations formed under the photolysis of 1,2,2,4-tetramethyl-1,2-dihydroquinoline in methanol and in a porous glass filled with methanol or dried in air or *in vacuo* were studied by the laser flash photolysis techniques. In MeOH, the carbocations recombine *via* the second-order law in the reaction with the MeO⁻ anion formed in an equimolar amount and decay *via* the first-order law in the reaction with the solvent with rate constants of $3 \cdot 10^8$ L mol⁻¹ s⁻¹ and $1.4 \cdot 10^3$ s⁻¹, respectively. When the solution is placed into the porous glass, no recombination of the carbocations with MeO⁻ is observed, and the reaction with the solvent is somewhat inhibited (rate constant $8 \cdot 10^2$ s⁻¹). More than tenfold inhibition of the reaction of the carbocations with methanol is observed on going to a monolayer of MeOH on the surface. The main route of carbocation decay in the porous glass dried *in vacuo* is the geminate recombination with the SiO groups. The corresponding kinetics is described in terms of the model of freely diffusing reactants.

Key words: laser photolysis, monolayer, dihydroquinoline, carbocation, porous glass, proton transfer, kinetics of geminate recombination.

The kinetics of fast reactions involving short-lived active species (electron-excited states, radicals, and others) in heterogeneous systems consisting of the solid inorganic surface and organic phase as a supported thin film is of interest because of the development of modern nanotechnologies.¹⁻³ Many organic molecules, including alcohols, can form ordered structures at the interface. They manifest new properties as compared to the initial liquid.^{4–10} Molecular organization in a thin organic layer at the interface is expected to exert a substantial effect on the kinetics of chemical processes. For instance, the recent studies of the kinetics of bimolecular diffusioncontrolled reactions of triplet-triplet annihilation and quenching of triplet states with molecular oxygen in thin alcohol films on the solid crystalline surface demonstrated several kinetic effects caused by molecular organization at the liquid-solid interface.¹¹⁻¹⁴ In these systems, the structurization of the medium affects the organization of transporting and spatial distribution of reacting particles. It was of interest to use the kinetics of a reaction directly involving molecules of the medium as a tool for studying the liquid-solid interface. Among these processes are the photogeneration of short-lived carbocations (CC) of alkylated 1,2-dihydroquinolines followed by the addition of an alcohol molecule or recombination with an alkoxy anion^{15–17} (Scheme 1).

Scheme 1



R = H, Me

The sensitivity of photolysis of 1,2-dihydroquinolines to the solvent composition has previously $^{16-19}$ been dem-

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onstrated in both the step of primary photophysical and photochemical processes producing a carbocation and the step of decay of the latter upon the addition of the solvent. In the present work, the efficiency of formation and the decay kinetics of a CC formed upon the photolysis of 1,2,2,4-tetramethyl-1,2-dihydroquinoline (TDHQ) in methanol and in the porous glass (PG), which was filled with methanol or dried in air or *in vacuo*, were studied by the nanosecond laser photolysis techniques.

Experimental

1,2,2,4-Tetramethyl-1,2-dihydroquinoline was synthesized by the reaction of 2,2,4-trimethyl-1,2-dihydroquinoline with trimethyl phosphate according to a standard procedure²⁰ in 71% yield, b.p. 131–132 °C (3 Torr). UV (MeOH), λ_{max}/nm (ε): 349 (2700), 290 (2000), 278 (2800), 232 (37000). ¹H NMR (CDCl₃), δ : 1.29 (s, 6 H); 1.98 (d, 3 H, J = 1.4 Hz); 2.79 (s, 3 H); 5.28 (d, 1 H, J = 1.4 Hz); 6.52 (dd, 1 H, H arom.); 6.65 (m, 1 H, H arom.); 7.06 (dd, 1 H, H arom.); 7.10 (m, 1 H, H arom.).

Absorption spectra and the decay kinetics of intermediate products in solutions and in the PG were recorded with the nanosecond laser photolysis technique at 400-800 nm using the procedure described elsewhere.²¹⁻²⁴ A PRA LN 1000 nitrogen laser (pulse duration 1 ns, irradiation wavelength 337 nm) operating in a frequency regime of 10 Hz was used as the excitation source. Kinetic curves were accumulated and averaged by 16-128 laser pulses using a Biomation 6500 high-performance analog-to-digital converter (USA) connected to a personal computer based on a Pentium processor (100 MHz). Each kinetic curve was transformed into a series of 1024 magnitudes, each of which corresponded to a time interval from 5 ns to 100 µs, depending on the duration of the process. The data presented in the work are average values obtained by the processing of at least ten kinetic curves under these conditions. The determination error of the kinetic characteristics did not exceed 20%. Measurements in solutions were carried out in a quartz cell with the 1-mm optical path length. All measurements were performed at 20 °C. Samples of a DV-1M sodium borosilicate glass $3 \times 4 \times 10$ mm in size, which were pre-alkalized for 0.5 h in a 0.05 M aqueous solution of NaOH at 50 °C and then kept for 72 h in a 0.1 M aqueous solution of HCl, were used in experiments with the PG. This procedure gave the PG with an average pore diameter of 8 nm, surface area of 80 m² cm⁻³, and porosity of 28% with respect to water.^{24–26} Before the PG was filled with the working solutions, it was evacuated for a long time at 50 °C to remove physically adsorbed water. The amount of methanol in the PG pores was determined from its amount that would be in a trap cooled with liquid nitrogen after 20 PG samples were evacuated. The porous glass completely filled with MeOH contained 0.25 mL of MeOH per 1 cm³ of the PG. After the MeOH-impregnated PG was dried in air until the recovery of its transparency (10 min at 20 °C), the remaining amount of MeOH in the PG was 0.025 mL of MeOH per 1 cm³ of the PG. This corresponds to a MeOH monolayer in which the surface area occupied by one molecule is 0.25 nm^2 (radius ~0.3 nm), which is typical of alcohol monolayers. $^{4-10}$



Fig. 1. Absorption spectra of the intermediate products obtained by the laser photolysis of TDHQ in methanol (2 mmol L^{-1}) (1) and in the PG filled with the same solution (2) immediately after a laser pulse.

Results and Discussion

The pulse photoexcitation of solutions of TDHQ in methanol (2 mmol L⁻¹) produces an intermediate product, whose absorption spectrum contains a relatively broad band with a maximum at ~480 nm (Fig. 1), which is characteristic of the CC generated from 1,2-dihydro-quinolines.^{15–19} When comparing the absorption intensities of the CC at 480 nm in methanol and the triplet state of benzophenone at 525 nm in benzene (quantum yield 100%, molar absorption coefficient 7200 L mol⁻¹ cm⁻¹)²⁷ detected upon the laser photolysis of the corresponding solutions with the same absorbance at the excitation wavelength, we obtain the molar absorption coefficient of the CC equal to ~4000 L mol⁻¹ cm⁻¹ if the quantum yield of the CC is 40%.^{18,19}

The kinetics of CC decay is described by a law corresponding to parallel reactions of the first and second orders. The rate constant of the second-order reaction is $\sim 3 \cdot 10^8$ L mol⁻¹ s⁻¹ (Fig. 2). It can be assumed that the decay of the CC according to the second-order law is caused by their recombination with the methoxy anions, which are formed simultaneously with the CC in the photoinduced reaction of proton transfer between the excited state of TDHQ and methanol. The bimolecular character of the process indicates the recombination of free ions, because the recombination of ions in solution as ion pairs is described by different kinetic laws. The dynamics of these processes involving the carbocations in nonviscous liquids was observed in the picosecond time scale.²⁸ The resulting second-order rate constant is much lower than the diffusion limit, being of the same order as the known bimolecular reaction rate constants of the ethylphenyl and aryltropyl radicals with MeO⁻ and other nucleophilic ions,²⁹ as well as the rate constant of the reaction of the



Fig. 2. Experimental kinetic curves of decay of the intermediate products detected at $\lambda = 480$ nm upon the laser photolysis of TDHQ in methanol (2 mmol L⁻¹) (*I*); in the PG filled with the same solution (*2*); after this PG sample was dried in air (*3*) and subsequently evacuated (*4*). Lines are the result of approximation according to the law for parallel reactions of the first and second orders (*I*), monoexponential law (*2*), biexponential law (*3*), and the Gaussian distribution of the logarithm of the first-order rate constant (*4*).

CC generated from 1,2,2,4,6-pentamethyl-1,2-dihydroquinoline with azide ions.³⁰ An increase in the stability of the CC upon the introduction of electron-donor substituents decreases the rate constants of their reactions. Therefore, for these dihydroquinolines, no contribution of the bimolecular component was found, 16,17,30 because it should appear at high CC concentrations.

The rate constant of the first-order reaction is $1.4 \cdot 10^3 \text{ s}^{-1}$, which is higher than that for the CC generated from the earlier studied 1,2-dihydroquinolines, which have the electron-donor substituents in position 6 of the aromatic fragment (k = 790 and 80 s^{-1} for 6-ethoxy-1,2,2,4,6-pentamethyl- and 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinolines, respectively).^{16,17} By analogy to the reactions of the other carbocations studied,³¹ the first-order process corresponds to the reaction of the CC with MeOH molecules proceeding *via* the nucleophilic addition mechanism. Therefore, the introduction of electron-donor substituents is accompanied by the stabilization of the CC and a decrease in the rate constants of the reactions of molecular and ionic nucleophiles with the CC, respectively.

The pulse photoexcitation of the PG filled with a solution of TDHQ in methanol generates the CC, which have almost the same absorption spectra and yield as those generated in the absence of the PG (see Figs 1 and 2). However, the kinetics of CC decay in a methanol solution incorporated in the PG pores strictly follows the firstorder law with a rate constant of $8 \cdot 10^2 \text{ s}^{-1}$ even at the initial CC concentrations $\geq 1 \cdot 10^{-4} \text{ mol L}^{-1}$. Thus, it can be assumed that the CC and/or MeO⁻ are adsorbed on the PG surface, which decreases considerably the rate constant of their recombination. The adsorption of the CC on the surface results in a noticeable (1.5-fold) inhibition of the reaction of the CC with methanol.

If the PG filled with a methanol solution of TDHO is dried in air for 10 min, the yield of the CC decreases and its decay kinetics changes sharply and is not described by the monoexponential law (see Fig. 2). The initial slope corresponds to a high rate constant: $-5 \cdot 10^3$ s⁻¹. About half of the CC decay very slowly with the time >20 ms (the upper time limit of the detection system). It should be expected that the methanol monolayer formed on the PG surface after passive drying, most likely, is not homogeneous. The presence of the fast component indicates that the monolayer contains regions of TDHQ localization where the CC decay very efficiently (by 10 times more rapidly than in the bulk) through, most likely, geminate recombination with the corresponding anions (see further). At the same time, the main effect of going to a monolayer on the surface is a considerable (more than tenfold) inhibition of the reaction of the CC with molecules of the environment. This can be assumed to relate to the structurized character of the monolayer in which the hydroxy groups of the methanol molecules, which are involved in the reaction, are linked through hydrogen bonds with the silanol groups on the surface.

Further drying of the PG by prolong (for 0.5 h) evacuation is not accompanied by a change in the yield of the CC but exerts a substantial effect on the kinetics of its decay, which becomes polychromatic (see Fig. 2). The initial slope corresponds to the very high rate constant: $\sim 1 \cdot 10^5 \text{ s}^{-1}$. During the time >20 ms (time constant of the detection system), 10% CC disappear. As a result of the prolong evacuation of the PG, physically adsorbed methanol is removed and a very heterogeneous disordered surface covered by silanol groups is formed. Polychromaticity of kinetic curves of various chemical processes on the porous silicate surface is a widely abundant phenomenon. One of the approaches to the quantitative description of the kinetics of processes on the porous surface is the use of the equation, which is obtained from the Gaussian distribution of the logarithm of the first-order rate constant³²

$$C_t/C_0 = \sqrt{\pi} \int_{-\infty}^{\infty} \exp(-x^2) \exp[-k_{\rm av} t \exp(\gamma x)] dx , \qquad (1)$$

where C_t and C_0 are the current and initial concentrations, respectively; k_{av} is the average value of the firstorder rate constant; γ is the distribution half-width. Using Eq. (1), one can satisfactorily describe the kinetics of CC decay in the dry PG in the initial time interval below 1 ms (see Fig. 2) at $k_{av} \approx 1 \cdot 10^5 \text{ s}^{-1}$ and a very broad distribution ($\gamma \approx 8$). The widths of the Gaussian distribution of the logarithm of the first-order rate constant for monomolecular and pseudo-monomolecular processes on the silicate porous surfaces are usually much smaller than those observed for the decay of the CC. The kinetic curves with a very broad distribution were observed on the porous surface for the decay of organic radical cations due to geminate recombination with the corresponding sites on the surface, which captured an electron during photoionization.^{33,34}

The kinetics of geminate recombination of pairs of freely diffusing reactants with the sum of the van der Waals radii σ , which were born at the distance *L* from each other and react with each other upon collisions with the probability α , is described by the equation³⁵

$$\frac{C_0 - C_t}{C_0} = \frac{\sigma\alpha}{L} \operatorname{erfc}\left[\frac{(1 - \alpha)\sigma}{2\sqrt{\pi Dt}}\right],\tag{2}$$

where *D* is the coefficient of mutual diffusion of the reactants. The kinetic curves of CC decay on the dry PG surface are well approximated by Eq. (2) in a rather wide time interval (Fig. 3) at $\alpha = 0.75$ and $D = 4.2 \cdot 10^{-12}$ cm² s⁻¹ when accepting that $\sigma = L = 0.7$ nm. The coefficient of mutual diffusion of the reactants is low, which is caused, most likely, by strong bonding with the surface. As a whole, the kinetic regularities observed indicate that the CC decay occurs on the evacuated surface *via* the recombination of the geminate pairs $-Si-O^--CC$.

Thus, the kinetics and mechanism of the reactions of the dihydroquinoline carbocations are very sensitive to the state of the inorganic surface—organic phase system.



Fig. 3. Kinetic curve of decay of the intermediate products detected at $\lambda = 480$ nm under the laser photolysis of TDHQ in the PG after evacuation (in the logarithmic time scale). Points are the superposition of three kinetic curves recorded in different time intervals (from 10 to 100 µs, from 10 µs to 1 ms, and from 10 µs to 1 ms), and the line is the result of approximation by Eq. (2) with allowance for the exponential apparatus function with time 20 ms.

The localization of a methanol solution of TDHQ in the system of pores of the finely porous borosilicate glass is accompanied by the adsorption of the CC on the surface with the molecular mobility loss and inhibition of the reaction of solvent addition, which results in the formation of the adducts. The sharp inhibition of this process is observed on going to a methanol monolayer on the surface, which is associated, most likely, with its structurization. The removal of physically adsorbed liquids from the surface by evacuation results in a situation when the geminate recombination with the anionic sites on the silicate surface becomes the main channel of CC decay.

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