

Effect of the Nature of Inert Solvent on the Decay Kinetics of the Carbocation Generated in the Photolysis of 1,2-Dihydroquinolines in Methanol¹

O. N. Lygo^a, T. D. Nekipelova^a, and E. N. Khodot^b

^a Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, 119334 Russia

^b Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia

e-mail: lygo@sky.chph.ras.ru

Received June 11, 2008

Abstract—The dependence of the quantum yield and the decay rate constant for the carbocation generated in the photolysis of 6-ethoxy-1,2,2,4-tetramethyl-1,2-dihydroquinoline (6-EtO-DHQ) in methanol on the solvent composition was studied in the mixtures of methanol with isopropanol, acetonitrile, and pentane by pulse photolysis. The addition of these solvents decreases the yield of the carbocation and differently affects the kinetic parameters of its decay. The carbocation decay in the mixtures MeOH-*i*-PrOH and MeOH-C₅H₁₂ is described by the pseudo-first order equation (k_1), with the dependence of k_1 having a maximum at 50 vol % of MeOH in the MeOH-*i*-PrOH mixtures, and k_1 increasing with a decrease in the MeOH concentration in the MeOH-C₅H₁₂ mixtures. In the MeOH-MeCN mixtures, the value of k_1 decreases with a decrease in the MeOH concentration, and, at the concentration of MeOH lower than 50 vol %, the contribution of the second-order reaction (k_2) is observed. The activation energies and preexponential factors were determined in the MeOH-C₅H₁₂ mixtures of different compositions, and it was shown that E_{act} practically did not depend on the solvent composition and were close to E_{act} for other carbocations obtained in MeOH. The increase in k_1 with a decrease in the MeOH concentration is caused by an increase in the preexponential factor. The results were discussed on the basis of the reaction mechanism involving the competing reactions of the carbocation combination with two nucleophilic particles, the MeOH molecule and the MeO[−] anion. The composition of the mixture and the nature of the inert solvent affect strongly the course of these reactions.

DOI: 10.1134/S0023158409030082

Carbocations are important intermediate species in the reactions of nucleophilic addition of molecular and ionic nucleophiles to olefins, and the investigation of their reactions is of a great interest for the organic chemistry [1–4]. Since the carbocations are active intermediates, their reactivity was determined from the ratio of the reaction products using two nucleophilic reagents, with the reactivity of one of those being known [2, 4, 5]. The development of the pulse methods for the investigation of intermediate species of chemical reactions made it possible to generate the carbocations in the photolysis of compounds with a general formula R-X, which under the action of light decompose heterolytically into an anion X[−] and a carbocation R⁺, and to determine directly the absolute values of the rate constants. A large variety of triphenyl- and diphenylmethyl carbocations were studied by this method [3, 6, 7].

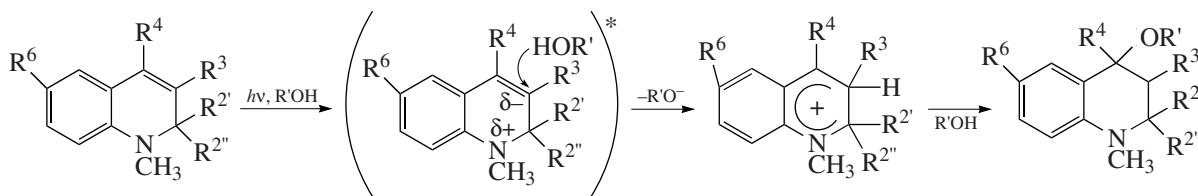
Recently, it has been shown that the photolysis of substituted 1,2-dihydroquinolines (DHQ) in protic solvents, methanol and water, proceeds via formation of the carbocation [8, 9], with the mechanism of its forma-

tion being principally different from the mechanism of the carbocation formation studied before (Scheme). In the case of DHQ, the formation of the carbocation occurs as a result of proton transfer from the protic solvent to the excited state of DHQ, and the alkoxy anion of the alcohol is formed as a counter ion.

The carbocation formed in the DHQ photolysis are convenient objects for the study of the features of these species by pulse photolysis: they have an absorption band in the visible region with $\lambda_{max} = 470$ –500 nm and are relatively stable. The lifetimes of these carbocations vary from hundreds μ s to hundreds ms in dependence on substituents in the aromatic ring and in the heterocycle and on the solvent [8, 9].

In this study, we compare the effect of the addition of inert solvents of different nature on the decay kinetics of the carbocation from 6-ethoxy-1,2,2,4-tetramethyl-1,2-dihydroquinoline (6-EtO-DHQ) in methanol. The carbocation from 6-EtO-DHQ is the most long-living from the carbocations studied earlier that determined its use in this study. The following inert solvents were used: nonpolar pentane (C₅H₁₂), polar acetonitrile (MeCN), and protic isopropanol (*i*-PrOH), which does not participate in the photoinduced proton transfer and

¹ The article was translated by the authors.



Scheme.

does not combine with the carbocation due to steric hindrance.

EXPERIMENTAL

Starting compounds. 6-Ethoxy-1,2,2,4-tetramethyl-1,2-dihydroquinoline (6-EtO-DHQ) was synthesized by *N*-methylation of the known antioxidant of ethoxyquin (6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline) with MeI. Methanol (Merck, for spectroscopy), pentane (Arcos Organics, pure), acetonitrile (Reakhim, pure for analysis) were used without additional purification.

Pulse photolysis. Decay kinetics of short-lived transient species, carbocations, was measured on a pulse photolysis setup with time resolution of 20 μ s. The samples were irradiated in quartz cells with an optic path length of 20 cm by a Xe lamp with a pulse energy of 150 J. The variations in the absorption 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 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 a maximum transmission at 365 nm. The transient absorption was recorded in the wavelength range from 400 to 600 nm with a pitch of 10 nm.

The processing of the experimental data obtained in the pulse photolysis experiments was carried out by a global kinetic analysis. The method suggests that all experimental absorption time curves registered at different wavelengths for the same solution are approximated by the same integral kinetic equation, with absorbance and rate constants being fitting parameters. The latters should be the same for the curves registered at all wavelengths, because refer to the same reactions, and the absorbance at different wavelengths characterizes the absorption spectra of corresponding transient species.

RESULTS AND DISCUSSION

The formation of the carbocation occurs with the participation of the MeOH molecules, therefore the decrease in the yield of the carbocation in the pulse photolysis of 6-EtO-DHQ was observed in all cases upon dilution of MeOH with the inert solvents (Fig. 1).

However, the character of the decrease in the carbocation yield is different for different solvents. The addition of the first 10 vol % of the inert solvent almost does not affect the yield in all cases. For pentane, the carbocation yield practically does not change up to 30 vol % of pentane, then drops rapidly, and, at the MeOH concentration lower than 20 vol %, the formation of the carbocation cannot be reliably registered (Fig. 1, curve 1). In acetonitrile, the substantial decrease in the carbocation yield is observed, when more than 10 vol % of the solvent is added (Fig. 1, curve 2), and the carbocation is generated in insignificant amount at the MeOH concentrations lower than 40 vol %. For isopropanol, the yield decreases slower than in the other solvents, but the carbocation is formed also in insignificant amount in this solvent at the MeOH concentration lower than 20 vol %. Due to the decrease in the carbocation yield upon dilution with the inert solvent, it is possible to study the kinetics of the carbocation decay only down to a definite MeOH concentra-

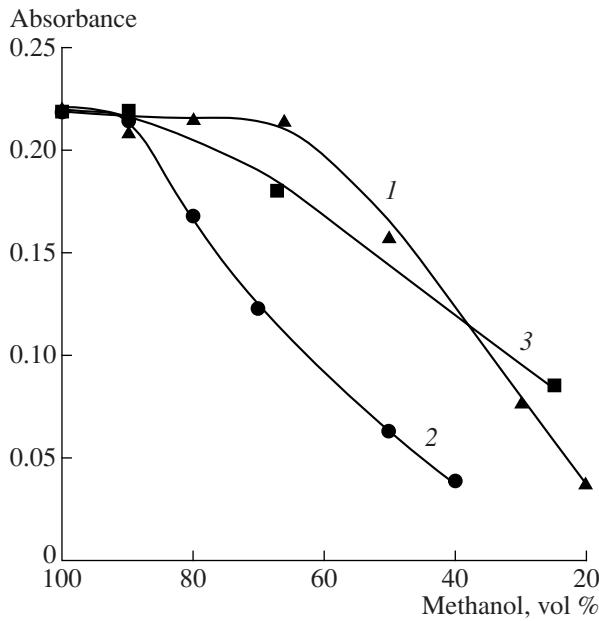


Fig. 1. The decrease in the yield of the carbocation from 6-EtO-DHQ ($\lambda_{\text{reg}} = 490$ nm) as a function of the solvent composition in mixtures (1) MeOH-C₅H₁₂, (2) MeOH-MeCN, and (3) MeOH-*i*-PrOH measured in the pulse photolysis experiments.

tion, and this limit is characteristic of the solvent each. At the MeOH concentrations below these limits, the formation of the carbocation is difficult to register because of its low concentration, and consequently, it is impossible to determine the rate constants of its decay.

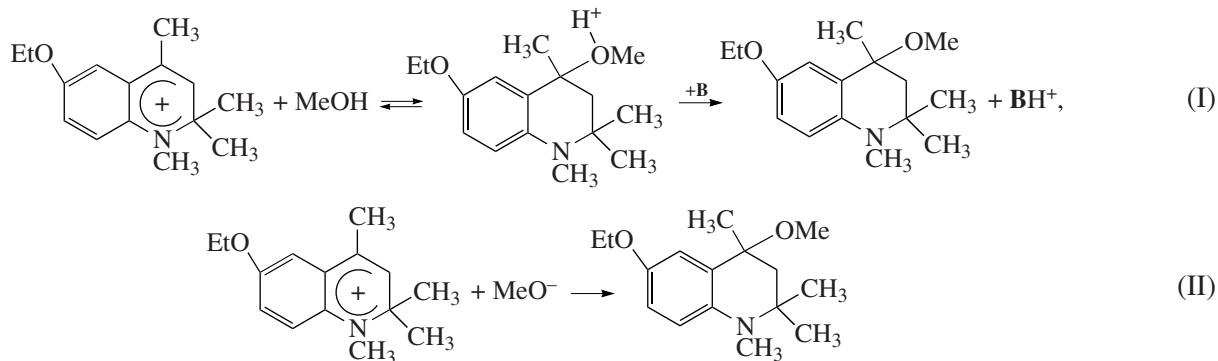
Earlier, it was shown for other DHQ that the carbocation is formed at the substantial excess of methanol or water in the mixtures, with this excess being different for different solvents added: this is the lowest for hexane and highest for acetonitrile [10, 11]. The photo-induced proton transfer to give the carbocation occurs in a MeOH cluster, therefore two factors are of a great importance in the case of mixtures: comparative solubility of DHQ in the components of the mixed solvent and the microstructure of the solvent. The solubility of DHQ is minimal in nonpolar alkanes, and MeOH already in small amounts forms cyclic and linear associates in these solvents [12]. These factors results in the fact that the DHQ molecules binding with MeOH by hydrogen bonds are localized in these associates. In acetonitrile, the formation of the MeOH clusters commences at substantially higher MeOH concentration. This fact as well as the high solubility of DHQ in MeCN results in the fact that the higher MeOH concentration is required for the generation of the carbocation. In the presence of isopropanol, the possibility of hydrogen bonding between all components of the mixture has additional influence.

The carbocation decay curves can be fitted to a first-order rate equation, with the rate constant of the carbocation decay from 6-EtO-DHQ in pure methanol being 95.4 s^{-1} . As methanol is diluted with an inert solvent, the behavior of k depends on the solvent nature (Fig. 2). As the isopropanol is added (to 60 vol % of MeOH), the reaction rate constant slightly increases (from 95 to 120 s^{-1}), and then decreases upon further decrease in the MeOH concentration (Fig. 2, curve 3).

Upon addition of pentane and acetonitrile, monotonous changes of the rate constant are observed in dependence on the methanol concentration, decreasing expectedly in acetonitrile (Fig. 2, curve 2) and surprisingly increasing in pentane, with a sharp increase in the rate constant at the MeOH concentration lower than 50 vol % (Fig. 2, curve 1). At MeOH concentration of 20 vol % in the mixture with pentane, the yield of the carbocation is low, therefore we managed only to estimate the rate constant of the carbocation decay at this MeOH concentration ($>900 \text{ s}^{-1}$), i.e., this increases almost by an order of magnitude in comparison with pure MeOH.

For the MeOH mixtures with isopropanol and pentane, the carbocation decay are adequately approximated by the equation for the first-order reaction over the whole range of the MeOH concentrations. Down to the MeOH concentration of 60 vol % in the mixtures with acetonitrile, the carbocation decay is also described by the equation for the first-order reaction; however, at 50 vol % of MeOH, the contribution of the second-order reaction is observed; and at 40 vol % of MeOH, the carbocation decay is adequately approximated by the equation for the second-order reaction (Fig. 3). Thus, with a decrease in the methanol fraction in acetonitrile, the change in the reaction order from the first order to the second order is observed for the decay of the carbocation generated from 6-EtO-DHQ in the pulse photolysis.

In the photolysis of 1,2-dihydroquinolines in methanol, there are two nucleophilic particles able to combine with the carbocation. These are methanol molecule (reaction (I)) and methoxy anion MeO^- (reaction (II)), which is generated simultaneously with the carbocation in the photoinduced proton transfer (Scheme).



Reaction (I) proceeds in two steps: the methanol molecule is added first, and then base **B** removes proton from the formed intermediate cation. In pure MeOH, the solvent by itself plays the role of the base. The contribution of reaction (II) is negligibly small in conventional pulse photolysis, and the carbocation decay

kinetics is described by the equation of the pseudo-first order. In the laser photolysis of 1,2,2,4-tetramethyl-1,2-dihydroquinoline in pure methanol [13], when the local concentration of the carbocation and the methoxy anion is substantially higher than in the conventional photolysis, the decay of the carbocation occurred in the bimo-

lecular reaction. In the case of the carbocation from 6-EtO-DHQ, the contribution of the second-order reaction was also observed with an increase in the pulse power ($k_2 = 3.7 \times 10^6 \text{ mol}^{-1} \text{ s}^{-1}$). The estimation show that the rate of combination reaction with MeOH is by a factor of 40 higher than the rate of the combination with the methoxy anion at the carbocation concentrations observed. Therefore, the process as a whole is described well by the equation for the first-order reaction. The presence of a maximum on the dependence of the decay rate constant for the carbocation from DHQ upon the addition of isopropanol is discussed in detail in [14, 15] and is caused by the higher proton affinity of isopropanol than methanol [16]. Therefore, after the reaction of the carbocation with methanol, isopropanol plays a role of the base and thus accelerates the formation of the final product. Upon further decrease in the MeOH concentration, the decrease in the concentration of the main reagent begins to play the role. Upon addition of acetonitrile, the expected decrease in the rate constant is observed, because the concentration of one of the reagent, methanol, decreases, and acetonitrile does not participate in the photolysis. The appearance of the contribution of the bimolecular reaction as the fraction of acetonitrile increases indicates the increase in the role of the methoxy anion in the carbocation decay. At the methanol concentration of 40 vol % (60 vol % of acetonitrile), reaction (II) becomes dominating. The bimolecular rate constant for reaction (II) at this acetonitrile concentration is $5.8 \times 10^7 \text{ mol}^{-1} \text{ s}^{-1}$, which is an order of magnitude higher than the corresponding rate constant in pure methanol. Such an increase in k_2 is caused by the inability of acetonitrile to hydrogen bonding, and as its fraction in the solvent mixture increases, the solvate shell of the ions formed in the reaction decreases. The decrease in the solvate shell decreases the energetic barrier for the interaction between MeO^- and the carbocation. As a result, the rate constant for the carbocation decay in reaction (II) increases. This increase in k_2 together with a decrease in the MeOH concentration makes reaction (II) competitive.

The activation energy for the decay of the carbocation from 6-EtO-DHQ was measured for the solutions in pure methanol and with addition of 30 and 70 vol % pentane in the temperature range from 10 to 25°C (table, Fig. 4). The calculated values are only appraisals, because the temperature range was not wide enough. However, there is no possibility to expand this, because the solubility of methanol in pentane decreases at lower temperatures, and the mixture begins to stratify; and at higher temperatures, pentane evaporates intensely. Nevertheless, these results indicate that the increase in the pseudo-first-order rate constant for the carbocation decay k_1 with a decrease in the reagent (MeOH) concentration in the mixture with pentane is not the result of the change in the mechanism of the addition reaction, because the activation energies for the mixtures with different MeOH concentration are

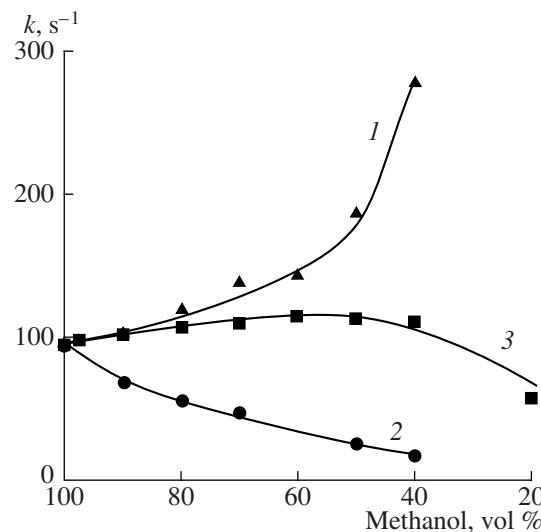


Fig. 2. The decay rate constant for the carbocation from 6-EtO-DHQ as a function of the solvent composition in the mixtures (1) $\text{MeOH}-\text{C}_5\text{H}_{12}$, (2) $\text{MeOH}-\text{MeCN}$, and (3) $\text{MeOH}-i\text{-PrOH}$.

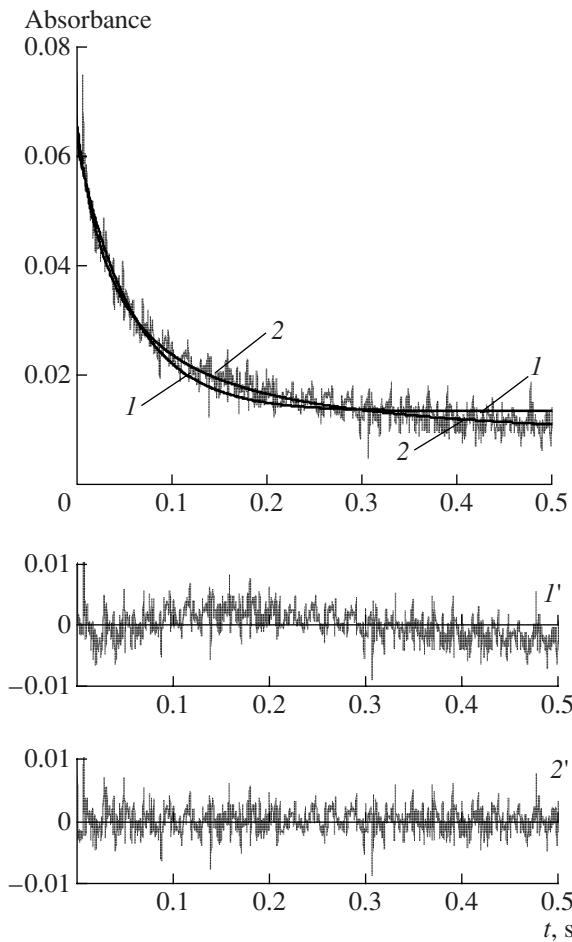


Fig. 3. The decay curve for the carbocation from 6-EtO-DHQ in the solvent mixture MeOH (40 vol %)– MeCN (60 vol %) registered in the pulse photolysis at $\lambda_{\text{reg}} = 470 \text{ nm}$ and fitting curves for (1) the first-order and (2) the second order decay; residuals for (1') the first-order and (2') second order decay curves.

The activation energy and preexponential factors for the decay of the carbocation from 6-ethoxy-1,2,2,4-tetramethyl-1,2-dihydroquinoline in the $\text{MeOH}-\text{C}_5\text{H}_{12}$ mixtures of different composition

[MeOH], vol %	E_{act} , kJ/mol	$A \times 10^{-8}$, s^{-1}
30	36 ± 4	8.8
70	36 ± 4	4.9
100	34 ± 3	1.2

almost the same (Fig. 4, table) and are close to the values of the activation energy for the decay of the carbocations generated in the photolysis of other DHQ in methanol (30–35 kJ/mol) [14, 15]. This indicates that the carbocation decay occurs in reaction (I) and the absence of the direct reaction with the MeO^- anion (reaction (II)).

The unusual dependence of k_1 on the MeOH concentration is the result of the drastic increase in the pre-exponential factor upon dilution of methanol with pentane (table). It should be pointed out that the values of A given in the table are effective, because the decrease in the MeOH concentration was not taken into account in their calculation. Taking this into account gives the higher difference in A for the mixtures with pentane in comparison with pure methanol, because the concentration of methanol is involved in the expression for the rate constant of the pseudo-first-order reaction. Methanol is miscible with pentane in any ratio forming associates with hydrogen bonds. The 6-EtO-DHQ molecules are involved in these associates, and as was men-

tioned above, these are these associates, where the proton transfer reaction occurs and the two charged species, the carbocation and the MeO^- anion, are formed. These species do not exit into the bulk nonpolar solvent. As the fraction of pentane increases, the solvate shell from the methanol molecules around the ions formed in the reaction decreases. In other words, the probability of the MeO^- participation in reaction (I) as the base **B** increases, because MeO^- anion is the most efficient base in this system. It is worth noting that the change in the mechanism of the formation of the DHQ carbocations in comparison with the well-known in the literature the carbocation formation in the photoinduced heterolytic bond scission results in the fact that the recombination of the ions generated in the primary contact ion pair can be neglected. This is confirmed experimentally on the basis of closeness of the quantum yields of the carbocations and the final product in the steady-state photolysis. If the recombination in the primary contact ion pair contributed in the formation of the final product, the quantum yield of the product should be higher than the carbocation quantum yield.

Thus, it is demonstrated in this study that the addition of the inert solvents of different nature does not alter the principal mechanism of the photolysis of 6-ethoxy-1,2,2,4-tetramethyl-1,2-dihydroquinoline in methanol, but affects strongly the kinetic parameters of the reaction due to the contribution of individual solvation effects relevant to each of these solvents, and microstructural peculiarities of the mixtures.

ACKNOWLEDGMENTS

The work was supported by the Program no. 1 of the Department of Chemistry and Material Sciences of the Russian Academy of Sciences “Theoretical and Experimental Research of the Nature of Chemical Bond and the Mechanisms of the Most Important Chemical Reactions.”

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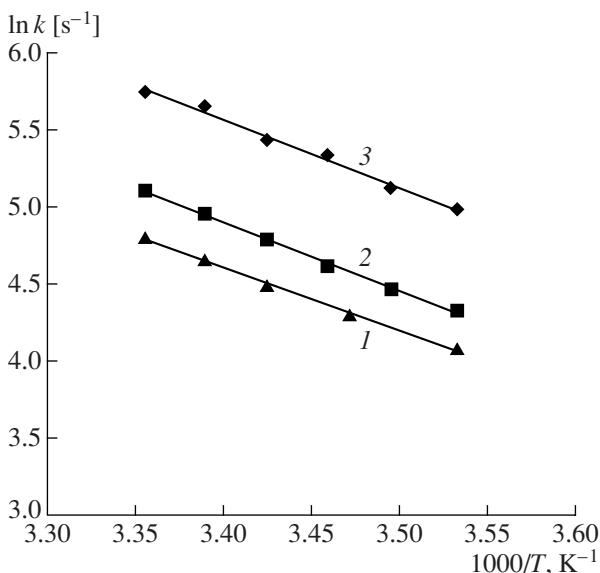


Fig. 4. The temperature dependence of the decay rate constant for the carbocation from 6-EtO-DHQ in (1) MeOH and the $\text{MeOH}-\text{C}_5\text{H}_{12}$ mixtures, pentane concentration (vol %): (2) 30 and (3) 70.

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