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# Reactivity of Carbocations from 1,2-Dihydroquinolines in Binary Mixtures of Methanol with Pentane and Acetonitrile

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**Abstract**—The rate constants and activation parameters of the reactions of the carbocation resulting from 6-ethoxy-1,2,2,4-tetramethyl-1,2-dihydroquinoline photolysis with methanol ($k_1$) and the methoxide ion ($k_2$) have been measured by flash photolysis in binary mixtures of methanol with inert solvents (nonpolar pentane and polar acetonitrile) in wide composition ranges. The changes in the activation parameters for $k_1$ at different solvent compositions show that the increase in the rate constant in the pentane mixtures is mainly determined by the increase in the preexponential factor. The decrease in $k_1$ in the acetonitrile mixtures is determined by the decrease in the methanol concentration and by the increase in the activation energy. The different roles of the methoxide ion in the reaction are demonstrated. They depend on the nature of the inert solvent in the mixture. The results of this study are considered in terms of methanol clustering in pentane and acetonitrile, the different solubilities of 6-ethoxy-1,2,2,4-tetramethyl-1,2-dihydroquinoline in the components of the binary mixtures, and the difference in distribution and solvation between the carbocation and the methoxide ion in the mixtures.

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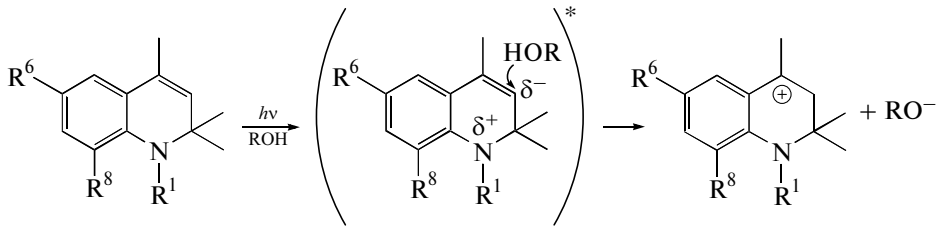
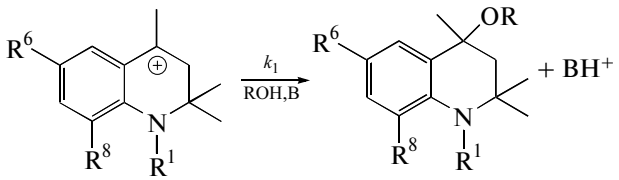
Many organic reactions are an interaction between an electrophile and a nucleophile. Carbocations are important electrophilic intermediates in most of these reactions, including solvolysis, which has been extensively investigated since the 1940s [1–7]. The development of flash techniques has made it possible to study short-lived carbocations and their reactions with nucleophiles by direct methods [8].

The photolysis of 2,2,4-trimethyl-1,2-dihydroquinolines with various substituents in 1-, 6-, and 8-positions in water and in methanol produces carbocations (reaction (I)). The reaction occurs due to proton transfer from the solvent to the excited state of 2,2,4-trimethyl-1,2-dihydroquinoline with a high quantum yield (0.2–0.4) [9, 10].

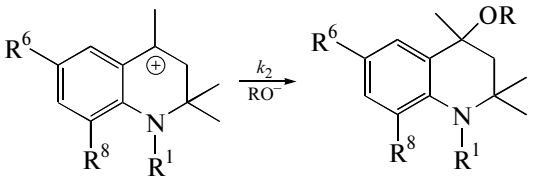



(I)

Carbocations react with water and alcohols to form the corresponding 4-hydroxy- or 4-alkoxy-1,2,2,4-tetrahydroquinolines in an almost quantitative yield (reaction (II)). The reaction between the carbocation and the anion $RO^-$ yielding the same reaction product is also possible (reaction (III)).



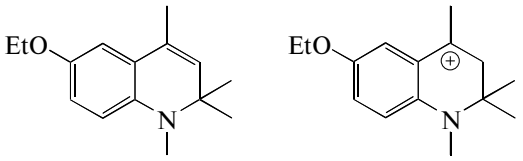

(II)




(III)

The formation of carbocations in the photoinduced proton transfer has several advantages over conventional heterolytic R–X bond cleavage [8]. The first of them is that the backward reaction is impossible, because the carbocation in the ground state forms from the excited state of the precursor. The counterions (alkoxide or hydroxide) resulting from proton transfer from the solvent cannot abstract a proton from the carbocation to form the initial 2,2,4-trimethyl-1,2-dihydroquinoline and cannot enter the recombination reaction in the primary contact ion pairs to form the reaction product because the orientation of the ions is inappropriate for their recombination. Under the conditions of standard flash photolysis in undiluted alcohols, the contribution of reaction (III) can be neglected. The basicity of the medium is significant for reaction (II) [7]. This is particularly true for the reactions conducted in alcohol–alcohol and alcohol–water mixtures. In this case, the addition of a more basic component, for instance, isopropanol, sharply accelerates the reaction, although this alcohol is not directly involved in the proton transfer reaction or in addition to the carbocation because of steric hindrance [11–13].

In this work, we continued to study the behavior of the carbocations from 2,2,4-trimethyl-1,2-dihydroquinolines in binary solvents consisting of methanol and an inert component (nonpolar pentane or polar acetonitrile). As was shown earlier [13], for carbocation **2** formed from 6-ethoxy-1,2,2,4-tetramethyl-1,2-dihydroquinoline **1**, the dilution of methanol with these solvents results in opposite effects: pentane accelerates the reaction, while acetonitrile causes the expected slowdown of the reaction.




**1** **2**

Here, we report the rate constants and activation parameters for reactions (II) and (III) in MeOH–MeCN mixtures of different compositions and refined activation parameters for the reaction in MeOH–$C_5H_{12}$ mixtures. The role of the methoxide ion in the reaction and the influence of the microstructural properties of the mixtures on the reactivity of the carbocations from 2,2,4-trimethyl-1,2-dihydroquinolines is elucidated.

## EXPERIMENTAL

**Starting chemicals.** 6-Ethoxy-1,2,2,4-tetramethyl-1,2-dihydroquinoline (**1**) was synthesized by the N-methylation of the known antioxidant ethoxyquin (6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline) with MeI. Methanol (Merck, for spectrophotometry), pentane (Arcos Organics, pure), and acetonitrile (Reakhim, analytical grade) were used as received.

**Flash photolysis.** The decay kinetics of short-lived intermediate species (carbocations) was measured by a flash photolysis technique with a time resolution of 20 μs. Samples were irradiated in quartz cells with an optical length of 20 cm using a Xe lamp with a flash energy of 150 J. The cell was provided with a water jacket, which made it possible to carry out measurements at different temperatures. In the MeOH–$C_5H_{12}$ mixtures, photolysis was carried out at 10–25°C. In the MeOH–MeCN mixtures, photolysis was carried out at 10–50°C. Changes in absorption were detected using a system consisting of a Xe lamp (75 W), a ZMP-3 monochromator, a photomultiplier, and an oscilloscope based on a PCI Bordo 211 digital array and a PC. To excite the long-wavelength absorption band of 2,2,4-trimethyl-1,2-dihydroquinoline, the exciting light was passed through a UFS-5 filter (300–400 nm bandpass range, transmission maximum at 365 nm). Transient absorption was measured in the wavelength range from 400 to 600 nm with 10-nm increments.

**Processing of the experimental data** obtained by flash photolysis was performed by global kinetic analysis. In this method, all time profiles of absorbance recorded at different wavelengths for the same solution are fitted to the same integral kinetic equation, and the values of absorbance and rate constants serving as fitting parameters. The rate constants should be equal for all curves since they refer to the same reactions, and the absorbances recorded at different wavelengths characterize the absorption spectra of the corresponding transient species. The decay rate of the carbocation resulting from the flash photolysis of **1** changes according to Eq. (1), where the decay of the carbocation in reaction (II) is described by the first-order rate law with respect to [**2**]. The MeOH concentration is included in the rate constant $k_1$ because [MeOH] exceeds the carbocation concentration by several orders of magnitude ([**2**] ≈ $10^{-6}$ mol/l). The second term in Eq. (1) refers to reaction (III) and is described by the second-order rate law with respect to [**2**] since the carbocation and $MeO^-$ result from photolysis at equal concentrations and, in data processing, [$MeO^-$] can be replaced with [**2**]:

$$d[\mathbf{2}]/dt = k_1[\mathbf{2}] + k_2[\mathbf{2}]^2. \quad (1)$$

Integration of Eq. (1) gives the following time dependence of [**2**]:

$$[\mathbf{2}] = [\mathbf{2}]_0 k_1 \exp(-k_1 t)/(k_1 + [\mathbf{2}]_0 k_2 - [\mathbf{2}]_0 k_2 \exp(-k_1 t)). \quad (2)$$

**Table 1.** First-order reaction rate constants for the carbocation decay ($k_1$) in the MeOH–MeCN and MeOH–$C_5H_{12}$ mixtures of different compositions at different temperatures

| [MeOH], vol % | $k_1$, $s^{-1}$ | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | MeOH–MeCN | | | | | | | | | MeOH–$C_5H_{12}$ | | | | | |
| | temperature, °C | | | | | | | | | temperature, °C | | | | | |
| | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 10 | 13 | 16 | 19 | 22 | 25 |
| 100 | 58 | 73 | 95 | 121 | – | – | – | – | 352 | 58 | – | 73 | 88 | 104 | 121 |
| 95 | 49 | 64 | 85 | 104 | 131 | 162 | 199 | 244 | 295 | – | – | – | – | – | – |
| 90 | – | 58 | 73 | 94 | 118 | 149 | 181 | 223 | 279 | – | – | – | – | – | – |
| 80 | 33 | 43 | 57 | 73 | 92 | 116 | 150 | 182 | 231 | – | – | – | – | – | – |
| 70 | – | – | – | – | – | – | – | – | – | 75 | 86 | 100 | 118 | 141 | 164 |
| 60 | 17 | 24 | 33 | 43 | 52 | 67 | 79 | 102 | 134 | – | – | – | – | – | – |
| 50 | 13 | 16 | 24 | 28 | 45 | 58 | 71 | 85 | 120 | – | – | – | – | – | – |
| 30 | – | – | – | – | – | – | – | – | – | 144 | 168 | 207 | 240 | 284 | 335 |

Equation (2) degenerates into Eq. (3) (first-order decay) at $k_1 \gg k_2[\mathbf{2}]$ and to Eq. (4) (second-order decay) at $k_1 \ll k_2[\mathbf{2}]$:

$$[\mathbf{2}] = [\mathbf{2}]_0 \exp(-k_1 t), \quad (3)$$

$$[\mathbf{2}] = [\mathbf{2}]_0/([\mathbf{2}]_0 k_2 t + 1). \quad (4)$$

The error in the rate constants determined in this way does not exceed 10%.

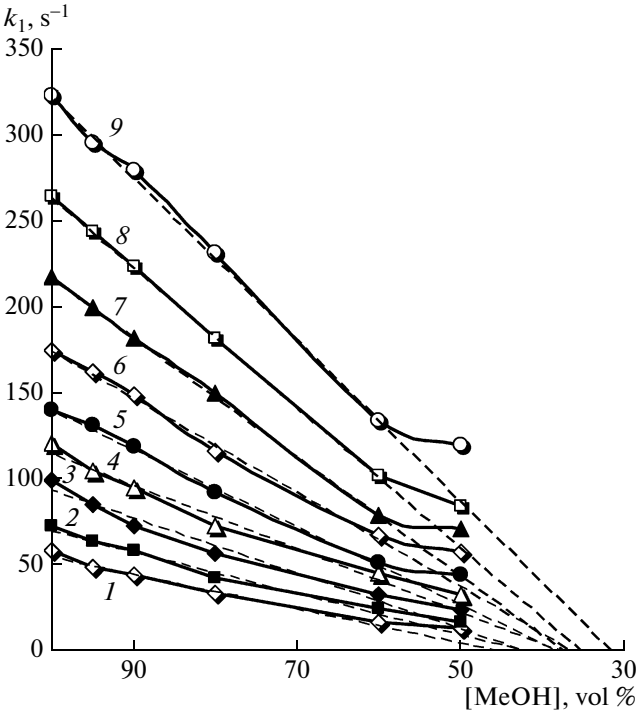



**Fig. 1.** First-order rate constant ($k_1$) of the carbocation decay in the MeOH–MeCN mixture versus the solvent composition at (*1*) 10, (*2*) 15, (*3*) 20, (*4*) 25, (*5*) 30, (*6*) 35, (*7*) 40, (*8*) 45, and (*9*) 50°C.

## RESULTS AND DISCUSSION

As was shown earlier [13], the lowest concentration of MeOH in the binary mixtures of methanol with $C_5H_{12}$ and MeCN (at which **2** forms from **1**) is 20 and 30 vol %, respectively. For this reason, the carbocation decay kinetics was studied at methanol contents exceeding these values. The decay kinetics of carbocation **2** at these MeOH concentrations and different temperatures (10–25 and 10–50°C for the mixtures of MeOH with $C_5H_{12}$ and MeCN, respectively) depends on the inert solvent. In the MeOH–$C_5H_{12}$ mixtures, the decay of the carbocation obeys the first-order rate law in the entire range of methanol concentrations and, as was mentioned above, the rate constant increases with a decrease in the reactant (MeOH) concentration (Table 1).

For the MeOH–MeCN mixtures, there is a contribution from the second-order reaction at [MeOH] = 60 vol % and below. At [MeOH] = 40 vol %, the carbocation decays exclusively via the second-order reaction. The first-order rate constant ($k_1$) decreases almost linearly with a decrease in [MeOH] at 100 vol % ≤ [MeOH] ≤ 60 vol % (Table 1, Fig. 1). However, the rectilinear dependences of $k_1$ on [MeOH] do not pass through the point of origin, but intersect the abscissa axis somewhere between 30 and 45 vol %, and the intercept increases as the temperature decreases. This means that the MeOH concentration active in the reaction with **2** is lower than the formal concentration of MeOH in MeCN.

The rate constant of the bimolecular decay of **2** ($k_2$) measured in the MeOH–MeCN mixtures increases with a decrease in [MeOH] ($0.94 \times 10^6$, $3.26 \times 10^6$, and $25.4 \times 10^6$ l mol$^{-1}$ s$^{-1}$ for [MeOH] = 100, 60, and 40 vol %, respectively, at 20°C). Note that the value of $k_2$ in pure MeOH was measured at a high flash energy such that the concentrations of **2** and methoxide ion are increased. Estimates show that the contribution from

the bimolecular reaction in pure MeOH is lower than 1% under the conditions of the present study, and this is confirmed by the carbocation decay following the first-order law at high [MeOH].

It has recently been demonstrated that photoinduced proton transfer in dihydroquinolines occurs in a substrate–alcohol complex and the number of methanol molecules in this complex larger than six ($n$(MeOH) ≥ 6) [14]. Therefore, at the instant of their formation, the carbocation and $MeO^-$ are in a solvation shell of methanol molecules. This solvation shell has different compositions in binary mixtures of MeOH with inert solvents, depending on the polarity of the latter. The MeOH molecules in binary mixtures are associated to form linear, branched, and cyclic polymer chains [15–19]. In the MeOH–$C_5H_{12}$ mixtures, the clusters are built exclusively from methanol molecules and the 1,2-dihydroquinoline molecules form complexes with methanol molecules and clusters already at relatively low [MeOH] values. This is explained by the preferencial solvation with methanol via hydrogen bond formation and by the low solubility of 2,2,4-trimethyl-1,2-dihydroquinolines in hydrocarbons [14]. In the MeOH–MeCN mixtures, one or two MeCN molecules can be involved in a MeOH cluster [16–19]. The solvation shell of 1,2-dihydroquinolines consists of molecules of both components, and the number of MeCN molecules in the solvation shell increases with a decrease in the MeOH concentration.

The changes observed in the decay rate constants of **2** in the binary mixtures are due to two decay reactions, namely, combination with MeOH (reaction (II)) and with $MeO^-$ (reaction (III)). The formation of various MeOH aggregates, the solvation of ions, and the ability of the ions resulting from photolysis (carbocation and methoxide ion) to separate away in these binary mixtures should be taken into account here. In the MeOH–$C_5H_{12}$ mixtures in the concentration range examined in this work, the polymer clusters of MeOH are dominant and, as was mentioned above, all molecules of **1** are hydrogen-bonded to these clusters [14]. The ions generated by photolysis are solvated with MeOH and cannot escape into the bulk of the nonpolar solvent pentane. Moreover, the absence of second-order decay is evidence that the two ions have a common solvation shell. The lower the MeOH concentration, the thinner and denser the shell. The compensation effect observed for these solutions (Table 2, Fig. 2) means that the increase in the carbocation decay rate constant is not a consequence of the change in the reaction mechanism. However, the dense configuration of the reactants (carbocation and MeOH) leads to a greater increase in the preexponential factor than in the activation energy, thus increasing the decay rate constant with dilution. In the case of the MeOH–$C_5H_{12}$ mixtures, the MeOH concentration is not explicitly included in the kinetic equation and in the rate constant $k_1$, because the MeOH concentration is almost constant near the carbocation and affects the rate constant through the value of the preexponential factor. The increase in $k_1$ at low MeOH concentrations in small MeOH clusters is due to the increasing role of $MeO^-$ as the base B in reaction (II) inside this cluster.

**Table 2.** Activation energy and preexponential factor for the first-order decay reaction of carbocation **2**

| [MeOH], vol % | $E_a$, kJ/mol | ln$A$ [$s^{-1}$] |
|---|---|---|
| MeOH–$C_5H_{12}$ | | |
| 30 | 39.3 | 21.7 |
| 70 | 37.0 | 20.1 |
| 100 | 34.3 | 18.7 |
| MeOH–MeCN | | |
| 95 | 33.6 | 18.3 |
| 90 | 34.5 | 18.5 |
| 80 | 36.7 | 19.1 |
| 60 | 39.0 | 19.7 |
| 50 | 42.0 | 20.5 |

The different situation observed in the MeOH–MeCN mixtures is due to the formation of looser clusters containing MeOH and MeCN molecules and the possibility of the forming ions escaping from these clusters to the bulk of the polar solvent. Owing to the good solubility of **1** in both solvents, the photoactive complex between **1** and MeOH in the MeOH–MeCN

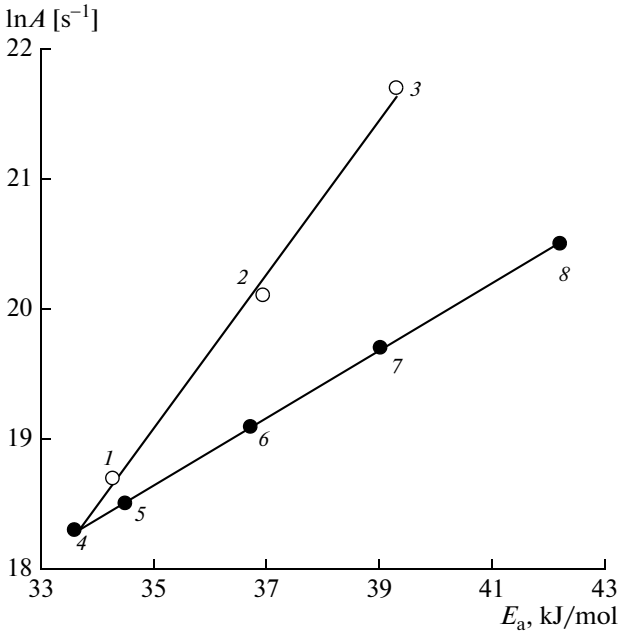



**Fig. 2.** ln $A$ versus $E_a$ for the MeOH–$C_5H_{12}$ mixtures containing (*1*) 100, (*2*) 70, and (*3*) 30 vol % MeOH and for the MeOH–MeCN mixtures containing (*4*) 95, (*5*) 90, (*6*) 80, (*7*) 60, and (*8*) 50 vol % MeOH.

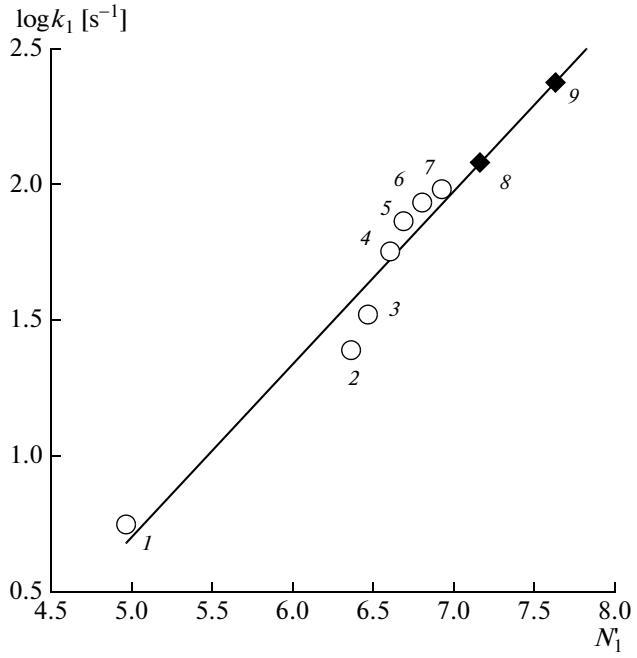



**Fig. 3.** Correlation between $\log k_1$ and $N_1'$ according to Eq. (5). The points correspond to the pure solvents and mixtures of different compositions: (*1*) $H_2O$; MeOH–MeCN mixture containing (*2*) 50, (*3*) 60, (*4*) 80, (*5*) 90, (*6*) 95, and (*7*) 100 vol % MeOH; and MeOH–$C_5H_{12}$ mixture containing (*8*) 70 and (*9*) 30 vol % MeOH. Points *8* and *9* are plotted on the correlation curve for the determination of $N_1'$ for these mixtures (see text). $T = 20°C$.

mixture forms at higher MeOH concentrations than the same complex in the MeOH–pentane mixture. The ions formed in this complex via photolysis escape readily to the solution bulk, and the reaction of the carbocation with MeOH and $MeO^-$ proceeds in the kinetic regime, controlled by the encounter of the reactants; i.e., its rate depends on the MeOH concentration. As was noted above (Fig. 1), the dependence of $k_1$ on the MeOH concentration indicates that the active concentration of MeOH is lower than the true concentration. We believe that, in this concentration range, the carbocation interacts with MeOH clusters rather than with free molecules. Interestingly, $k_1$ changes insignificantly as the MeOH concentration is decreased from 60 to 50 vol % (Fig. 1), indicating that the active concentration of MeOH changes slightly; i.e., the number of MeOH molecules in the cluster decreases. Unfortunately, at lower concentrations of MeOH the bimolecular reaction between **2** and $MeO^-$ becomes the main carbocation decay route and this does not allow one to determine $k_1$ at these methanol concentrations.

The strong dependence of the rate constant of the bimolecular reaction between **2** and $MeO^-$ ($k_2$) on the composition of the mixture is due to the influence of solvation on the rate of ion reactions [20, 21]. The lower the MeOH concentration, the thinner the solvation shell of both ions (carbocation and $MeO^-$) and the higher the rate constant of their reaction. Compound **2** is a comparatively weak electrophile, so this result is in agreement with the report that weak electrophiles interact more rapidly with alkoxide ions than with the corresponding alcohols at the alkoxide concentration 1–10 mmol/l [22]. Under our experimental conditions, the concentration of the ions is ~$10^{-6}$ mol/l and, hence, in pure alcohol solutions the reaction between the carbocation and $MeO^-$ cannot compete with the reaction between the carbocation and MeOH. As the MeOH concentration in MeCN decreases, $k_1$ decreases and $k_2$ increases. As a consequence, at [MeOH] = 60 vol % the rates of reactions (II) and (III) become comparable and, at [MeOH] = 40 vol %, reaction (III) becomes dominant.

To estimate the reactivity of the carbocations toward individual solvents and their mixtures, researchers conventionally use linear correlations between $\log k_1$ at 20°C and the nucleophilicity of the solvent and the electrophilicity of a particular carbocation [23–25]. Several nucleophilicity scales have been suggested, and this problem is considered in detail in recent publications [24, 26]. The rate constants $k_1$ for carbocation **2** in the MeOH–MeCN mixture (Table 1) and in water (5.6 $s^{-1}$ [27]) correlate satisfactorily with the nucleophilicity of the solvents. This correlation, obtained using Eq. (5) and nucleophilicity data for the mixtures ($N_1'$) [24], is presented in Fig. 3

$$\log k_1 = E + sN_1' + c, \qquad (5)$$

where $s$ is the parameter characterizing a particular electrophile in its interaction with nucleophiles, $E$ is the electrophilicity of the carbocation, and $c$ is the correction factor.

There are no literature data on the reactivity of the carbocations toward alcohols in their binary mixtures with alkanes or on the nucleophilicity of these mixtures. This is due to the fact that the carbocations are usually obtained by the heterolytic cleavage of the R–X bond under irradiation. The cation $R^+$ and anion $X^-$ generated in alcohol–alkane mixtures are in alcohol cluster and recombine rapidly in the primary ion pair, which makes it difficult to determine the reactivity of the carbocation toward alcohol in these mixtures. The carbocations of 1,2-dihydroquinolines result from proton transfer from the alcohol and, as mentioned above, their recombination with the alkoxide ion in the primary ion pair seems improbable. The increase in the rate constant in the MeOH–$C_5H_{12}$ mixtures with a decrease in the alcohol concentration formally implies an increase in the nucleophilicity of this mixture. The correlation presented in Fig. 3 shows that the estimated values of nucleophilicity for solutions containing 70 and 30 vol % alcohol in pentane are 7.2 and 7.6, respectively. It is noteworthy that the

parameter $s$ that characterizes the slope of the correlation is small: $s = 0.63$. In the case of the benzohydryl carbocations, for which most correlations were obtained, the $s$ changes from 0.5 to 1.25 on passing from strong to weak electrophiles [24]. Probably, the value of $s$ obtained for carbocation **2**, a relatively weak electrophile, reflects the specific features of the structure of this carbocation, which has two centers for hydrogen bonding with the solvent, namely, the nitrogen atom of the heterocycle and the oxygen atom of the ethoxy group.

Temperature-dependent rate constant data for the reactions of carbocations with nucleophiles are almost lacking in the literature [1]. The activation parameters for the reactions of the carbocations from various 1,2-dihydroquinolines with molecular and ionic nucleophiles were determined earlier [11, 12, 28]. In the present report, this investigation was continued for the mixtures examined. As follows from the temperature dependence of $k_1$ and from the activation parameters for the first-order decay reaction calculated from these dependences (Table 2), the dilution of MeOH with an inert solvent enhances both the activation energy and the preexponential factor, but the strength of the effect of these parameters on $k_1$ depends on the inert solvent. The compensation dependences for the two mixtures are different (Fig. 2). In the $C_5H_{12}$-containing mixtures, the increase in $k_1$ with dilution is due to the increase in the preexponential factor. In the MeCN-containing mixtures, the decrease in $k_1$ is accompanied by a greater increase in the activation energy. Interestingly, the point corresponding to pure MeOH lies in the compensation curve for the MeOH–$C_5H_{12}$ mixture and falls away from the same curve for MeOH–MeCN. It is likely that this fact reflects the difference between the aggregation behaviors of MeOH in polar and nonpolar solvents.

The temperature dependence of $k_2$ in the coordinates of the Arrhenius equation is not linear, and the activation energy and preexponential factor decrease with temperature (Fig. 4). The temperature dependence of $k_2$ fitted to two straight lines is plotted in Fig. 4, which shows that the activation energy decreases by a factor larger than 2 in the temperature range examined (53.5 and 25.4 kJ/mol for the temperature ranges of 10–30 and 30–50°C, respectively). It is likely that the decrease in the activation energy of reaction (III) with temperature is due to the more active molecular exchange between the solvation shells of ions at higher temperatures.

Thus, the strong effect of the polarity of the inert solvent in the binary mixture on the reactivity of the carbocation from **1** toward methanol is due to the difference in ion solvation. The way the activation parameters change shows that, in the MeOH–$C_5H_{12}$ mixtures, an increase in the preexponential factor leads to an increase in the rate constant with dilution, whereas in the MeOH–MeCN mixture, a decrease in the rate constant is accompanied by a larger increase in the activation energy. In the MeOH–$C_5H_{12}$ mixtures, the first-order rate constant $k_1$ increases with dilution due to the formation of a denser solvation shell of MeOH molecules, which is common for the carbocation and $MeO^-$, which cannot escape from this solvation shell to the bulk of the nonpolar solvent. The role of the counterion is reduced to the neutralization of the ionic intermediate resulting from the reaction between **2** and MeOH.

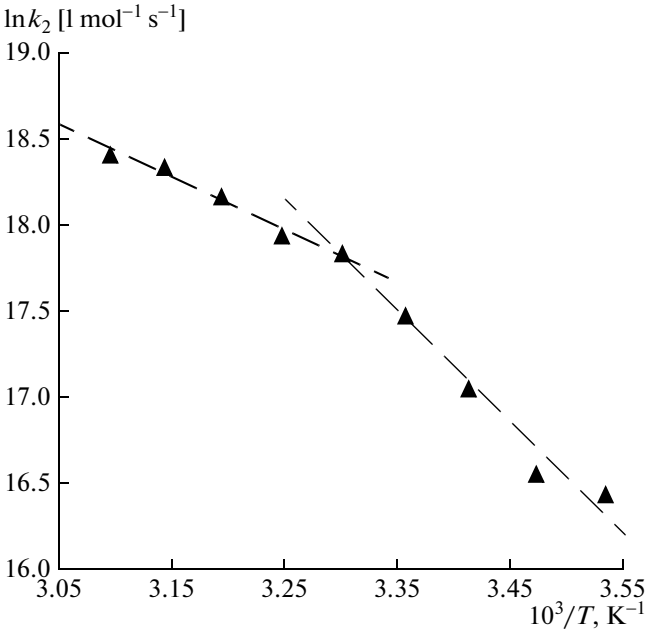



**Fig. 4.** Temperature dependence of $k_2$ in the Arrhenius coordinates for the MeOH–MeCN mixture at [MeOH] = 40 vol %.

In the MeOH–MeCN mixtures, the ions separate readily from one another after their formation, which is manifested as an increase in the role of the bimolecular reaction between **2** and $MeO^-$ with increasing dilution. The first-order rate constant decreases with dilution due to the decrease in the MeOH concentration, but the character of this decrease indicates that the active concentration of MeOH is lower than that in the mixture because of the formation of MeOH aggregates.

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## REFERENCES

1. Hawdon, A.R., Hughes, E.D., and Ingold, C.K., *J. Chem. Soc.*, 1952, p. 2499.
2. Olah, G.A., *J. Org. Chem.*, 2001, vol. 66, no. 18, p. 5943.

3. Richard, J.P., *Tetrahedron*, 1995, vol. 51, p. 1535.
4. Bentley, T.W., Jones, R.O., Kang, D.H., and Koo, I.S., *J. Phys. Org. Chem.*, 2009, vol. 22, p. 799.
5. Ritchie, C.D., *Acc. Chem. Res.*, 1972, vol. 5, p. 348.
6. Bunton, C.A., Del Pesco, T.W., Dunlop, A.M., and Yang, K.-H., *J. Org. Chem.*, 1971, vol. 36, p. 887.
7. Ta-Shma, R. and Rappoport, Z., *Adv. Phys. Org. Chem.*, 1992, vol. 27, p. 239.
8. McClelland, R.A., *Tetrahedron*, 1996, vol. 52, no. 20, p. 6823.
9. Nekipelova, T.D., *Photochem. Photobiol. Sci.*, 2002, vol. 1, no. 3, p. 204.
10. Nekipelova, T., Gostev, F., Kuzmin, V., and Sarkisov, O., *Photochem. Photobiol. Sci.*, 2006, vol. 5, no. 9, p. 815.
11. Nekipelova, T.D., Levina, I.I, and Shishkov, V.S., *Kinet. Katal.*, 2004, vol. 45, no. 1, p. 28 [*Kinet. Catal.* (Engl. Transl.), vol. 45, no. 1, p. 24].
12. Nekipelova, T.D., in *Chemical and Biological Kinetics: New Horizons*, Burlakova, E.B., Shilov, A.E., Varfolomeev, S.D., and Zaikov, G.E., Eds., Leiden: Brill, 2005, vol. 1, p. 241.
13. Lygo, O.N., Nekipelova, T.D., and Khodot, E.N., *Kinet. Katal.*, 2009, vol. 50, no. 3, p. 411 [*Kinet. Catal.* (Engl. Transl.), vol. 50, no. 3, p. 390].
14. Nekipelova, T.D., Kuzmin, V.A., Razumov, V.F., and Gak, V.Yu., *Khim. Vys. Energ.*, 2009, vol. 43, no. 5, p. 445 [*High Energy Chem.* (Engl. Transl.), vol. 43, no. 5, p. 391].
15. Durov, V.A., Iglesias, T.P., Shilov, I.Yu., and Moscalets, A.P., *J. Mol. Liq.*, 2008, vol. 138, no. 1, p. 40.
16. Reimers, J.R. and Hall, L.E., *J. Am. Chem. Soc.*, 1999, vol. 121, no. 15, p. 3730.
17. Stubbs, J.M. and Siepmann, J.I., *J. Am. Chem. Soc.*, 2005, vol. 127, no. 13, p. 4722.
18. Besnard, M., Cabaco, M.I., Strehle, F., and Yarwood, J., *Chem. Phys.*, 1992, vol. 163, no. 1, p. 103.
19. Farwaneh, S.S., Yarwood, J., Cabaco, M.I., and Besnard, M., *J. Mol. Liq.*, 1993, vol. 56, p. 317.
20. Ingold, C.K., *Structure and Mechanism in Organic Chemistry*, Ithaca, N.Y.: Cornell Univ., 1969.
21. Gordon, J., *The Organic Chemistry of Electrolyte Solutions*, New York: Wiley, 1975.
22. Phan, T.B. and Mayr, H., *Can. J. Chem.*, 2005, vol. 83, p. 1554.
23. Swain, C.G. and Scott, C.B., *J. Am. Chem. Soc.*, 1953, vol. 75, p. 141.
24. Bentley, T.W., *J. Phys. Org. Chem.*, 2010, vol. 23, no. 1, p. 30.
25. Minegishi, S., Kobayashi, S., and Mayr, H., *J. Am. Chem. Soc.*, 2004, vol. 126, p. 5174.
26. Bentley, T.W., *J. Phys. Org. Chem.*, 2010, vol. 23, no. 9, p. 836.
27. Nekipelova, T.D., *Kinet. Katal.*, 2008, vol. 49, no. 2, p. 231 [*Kinet. Catal.* (Engl. Transl.), vol. 49, no. 2, p. 218].
28. Nekipelova, T.D., Levina, I.I., Levin, P.P., and Kuzmin, V.A., *Izv. Akad. Nauk, Ser. Khim.*, 2004, p. 772.