Kinetics and Catalysis, Vol. 45, No. 1, 2004, pp. 24–30. Translated from Kinetika i Kataliz, Vol. 45, No. 1, 2004, pp. 28–34.
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Reactivity of Water and Alcohols toward Carbocations Generated in the Photolysis of 2,2,4,6-Tetramethyl-1,2-dihydroquinoline

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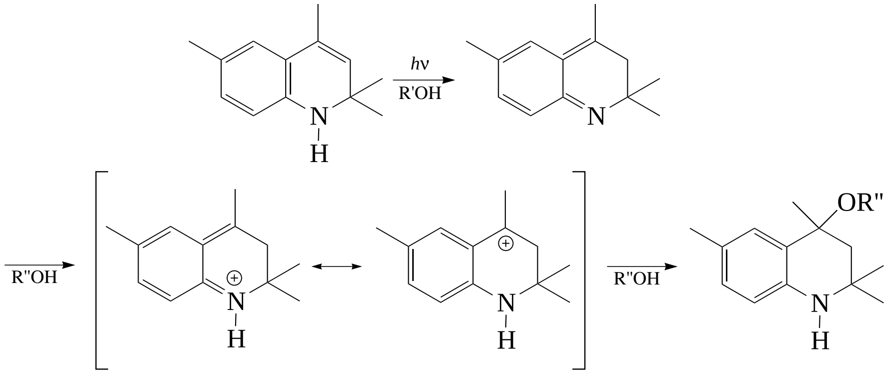
Received August 12, 2002

Abstract—The rate constants of the decay of carbocation generated in the photolysis of 2,2,4,6-tetramethyl-1,2-dihydroquinoline and the composition of reaction products were studied as a function of solvent composition in the mixtures H_2O–ROH and MeOH–ROH (R = Et, *n*-Pr, and *i*-Pr). The rate constants of carbocation decay in alcohols are more than 20 times higher than the corresponding rate constants in water. As follows from the composition of the products obtained in the photolysis in the alcohol–water mixtures, MeOH is only 1.4 times more reactive than water, and EtOH and *n*-PrOH are even less active than water. The inconsistency in the product composition in the mixtures and the values of the observed rate constants in these solvents was explained by the two-step mechanism of the reaction: the reversible formation of an adduct of the carbocation with the solvent components and subsequent proton transfer to the solvent to form the final product, with the first step determining the product composition and the second step determining the rate of carbocation decay. The relative rate constants of alcohols and water were determined for the two steps. The preferred solvation of the carbocation with water also contributes significantly to the reaction kinetics and the product composition in the water–alcohol solutions.

INTRODUCTION

Carbocations, active intermediates in various synthetic organic reactions and metabolic processes in living organisms, have attracted the attention of chemists and biochemists over more than a century, and the study of their chemical reactivity is still a topical problem of physical organic chemistry [1–7]. Development of experimental methods to determine the lifetimes of intermediate species as low as picoseconds made it possible to study not only carbocation formation reactions but also carbocation decay by both direct methods [3–6] and measuring the relative rate constants [3, 7].

Recently it has been shown that the photoinduced addition of water and alcohols to the double bond of a series of 2,2,4-trimethyl-1,2-dihydroquinolines (DHQ) occurs via the successive formation of two reactive intermediates according to Scheme 1 [8–12]:



R' = H, Me
R" = H, Me, Et, Pr

Scheme 1.

The first intermediate species, cyclic *ortho*-quinomethane imine, is a tautomer of initial DHQ and is formed via proton transfer in the excited singlet state of DHQ with the participation of the solvent. This species is protonated by the solvent to form a cation followed by nucleophilic addition of the solvent to form a final product. The two intermediate species lifetimes on a millisecond time scale and absorption spectra in the visible region (λ_{max} 420 and 480–500 nm, respectively). They are observed when the reaction is studied by conventional pulse photolysis [10–12]. Alcohols with the number of C atoms higher than one are involved in the reaction only in mixtures with H_2O and MeOH to give a mixture of adducts. Propanol-2 does not give an adduct because of steric hindrance. The presence of water and methanol is a necessary condition for proton transfer in the excited state. As expected, the rate constant of protonation of the first intermediate species with the solvent to form the carbocation decreases in the series H_2O > MeOH > EtOH.

The possibility of resonance stabilization of the carbocation as shown in Scheme 1 defines the features of this species: a high value of pK_a equal to 10.4 for 2,2,4,6-tetramethyl-1,2-dihydroquinoline (6-Me-DHQ) and long lifetimes (ca. 50 ms for 6-Me-DHQ in water at ambient temperature). The long lifetimes for the carbocations from DHQ and the ease of their formation and observation make these species attractive for the study of reactions of carbocations.

Recently we have found that the observed rate constant of the solvent combination with the carbocation from DHQ increases by more than an order of magnitude on passing from H_2O to MeOH [10–12]. In order to clarify the mechanism of the addition of water and alcohols to this transient species and to measure the rate constants of the combination of the carbocations with various alcohols, the rate constant of carbocation decay and the composition of photolysis final products were studied in this work as dependent on the solvent composition in the mixtures H_2O–ROH and MeOH–ROH (R = Et, *n*-Pr, and *i*-Pr).

EXPERIMENTAL

Starting materials. 2,2,4,6-Tetramethyl-1,2-dihydroquinoline (m.p., 42°C) (Reakhim) was sublimed in a vacuum before use. Methanol for spectroscopy (Merck), ethanol, *n*-propanol, isopropanol for spectroscopy (Reakhim) and doubly distilled water were used.

Isolation and identification of reaction products. Preparative-scale steady-state photolysis of solutions of 6-Me-DHQ ($(1–3) \times 10^{-3}$ mol/l, ~10 mg in 20 ml of a solution) was carried out in a glass (Pyrex) flask stirred with a magnetic stirrer by the full light of a DRSh-1000 mercury lamp. The long-wavelength absorption band was excited with the glass being a light filter ($\lambda_{max}(H_2O)$ = 335 nm, $\lambda_{max}(CH_3OH)$ = 343 nm, $\lambda_{max}(C_2H_5OH, C_3H_8OH)$ = 350 nm) [8, 9]. The reaction was controlled by spectrophotometry by periodically withdrawing aliquots into quartz cells with a light path length of 0.2 cm. The conversion of 6-Me-DHQ to the products occurred in water-alcohol and methanol solutions for ~2 h. When the reaction was complete, the solvent was removed by distillation in a vacuum at 20–25°C, and the solid fine-crystalline residue was analyzed without purification. The composition of final products was determined from ^{1}H NMR spectra of the products obtained by steady-state photolysis in the H_2O–ROH and MeOH–*n*-PrOH mixtures using the difference in the chemical shifts of the signals for protons in positions 3 and 5 of the hydroxy and methoxy adducts and in the position of the signal of methyl protons in methoxy- and propyloxy adducts [9].

The ^{1}H NMR spectra were recorded on a WM-250 Bruker spectrometer in $(CD_3)_2SO$ solutions with tetramethylsilane as a reference.

Pulse photolysis. The rate constants of the carbocation decay were determined by the pulse photolysis of 6-Me-DHQ solutions acidified with AcOH according to the procedure described elsewhere [10–12]. The samples were irradiated in a quartz cell with a light path length of 10 cm by an Xe lamp with a flash energy of 150 J. Changes in absorption were registered with a system consisting of an Xe lamp (75 W), a monochromator ZMP-3, and a photomultiplier connected with an S9-8 digital storing oscilloscope. The digitized data was processed with using a Pentium 200 PC. To excite the long-wavelength band of 6-Me-DHQ, a light beam was filtered with a UFS-5 filter (transmittance range 300–400 nm with a maximum transmittance at 365 nm).

RESULTS AND DISCUSSION

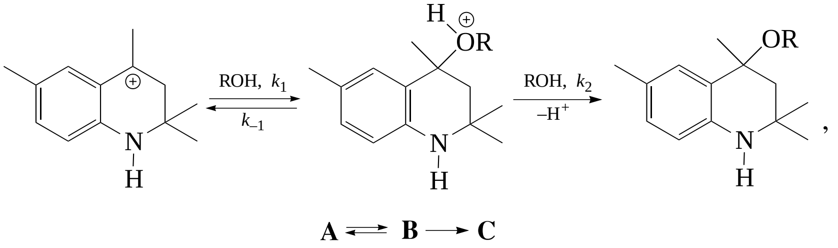
In the photolysis of DHQ in alcohol and aqueous solutions acidified with AcOH ([AcOH] > 1×10^{-5} mol/l), the lifetime of the first intermediate, cyclic *o*-quinomethane imine drastically drops, and only the formation of the carbocation is observed on a millisecond time scale [10]. The carbocation decay follows a first-order reaction. The observed values of the rate constants for the carbocation decay (k_{obs}) in different alcohols and water are listed in the table. Since the precursor of the carbocation is not generated upon photoexcitation of DHQ in pure EtOH and *n*-PrOH and the carbocation itself is not formed [8–10], the values of k_{obs} for these alcohols were obtained by extrapolation of the values of k_{obs} in the mixtures (Fig. 1). The value for *n*-PrOH was found to be the same in the mixtures with H_2O and MeOH. The values of k_{obs}^{ROH} for alcohols are close to each other but are more than 20 times higher than the rate constant in water k_{obs}^{aq} (see table) that corresponds to the higher nucleophilicity of alcohols compared to water. However, the selectivity of photolysis in the mixtures (the expression for the selectivity of this reaction will be given below, see Scheme 3 and Eq. (1)) is substantially lower than one might expect from the ratios between the rate constants (compare curves *2* and *4* in Fig. 2, table). As follows from the product analysis, Observed rate constants of the carbocation decay in pure solvents (k_{obs}), the selectivity of the addition of alcohols and water to 6-Me-DHQ (α), and the ratio of the rate constants of proton elimination (β) in the mixtures (18°C)

R'OH	R"OH	$k_{obs}^{R'OH}$, s^{-1}	$k_{obs}^{R''OH}$, s^{-1}	$k_{obs}^{R'OH}/k_{obs}^{R''OH}$	α**	β
MeOH	H_2O	540 ± 10	18 ± 1	30	1.4	22***
EtOH	H_2O	515 ± 10	18 ± 1	28.6	0.43	51***
n-PrOH	H_2O	477 ± 10	18 ± 1	26.5	0.43	49***
i-PrOH	H_2O	160 ± 5*	18 ± 1	9	–	51***
MeOH	*n*-PrOH	540 ± 10	477 ± 10	1.12	2.5	0.42
MeOH	*i*-PrOH	540 ± 10	560 ± 10*	0.96	–	0.43

*The highest value obtained in the mixture with *i*-PrOH. ** Calculated by Eq. (1). *** Calculated by Eq. (5).

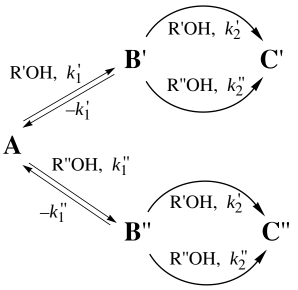
MeOH is only 1.4 times more active than water, and EtOH and *n*-PrOH are even less active than water. The latter observation conflicts with the higher nucleophilicity of these solvents compared to water [13] and is the result of steric interference during the formation of adducts with these alcohols. In fact, two isomers were observed in the ^{1}H NMR spectra of the adducts of EtOH and *n*-PrOH due to the hindered rotation of the alkoxy group added [8]. Probably, this is the reason for the 2.5 times higher activity of MeOH in the addition reaction than that of *n*-PrOH (Fig. 2, curve *3*).

In the alcohol mixtures (Fig. 1a), a synergy is observed when the k_{obs} of the mixture is higher than the k_{obs} of each alcohol. More surprising is an enhancement of k_{obs} in the mixtures with *i*-PrOH (Figs. 1a, 1b, curves *2*), which is inactive in the addition reaction. The seeming contradiction between the selectivity and the values of k_{obs} in various solvents, as well as the acceleration of carbocation decay in the presence of *i*-PrOH, can be reconciled if the mechanism of the reaction of the carbocation with a solvent is presented in the form



Scheme 2.

that is, the steps of the addition of ROH and the elimination of proton are separated. For the solvent mixture (R'OH + R"OH), this scheme takes the form



Scheme 3.

In this case, the product composition ([**C**']/[**C**"]) will be defined by the relationship

$$[\mathbf{C}']/[\mathbf{C}''] = \alpha X/(1 - X), \qquad (1)$$

where X and $(1 - X)$ are molar fractions of the solvent components R'OH and R"OH, respectively; the selectivity $\alpha = k_1'/k_1''$ when $k_{-1}^i \ll k_2^i$, and $\alpha = K_1'/K_1''$ when $k_{-1}^i \gg k_2^i$. In the case under consideration, all measurements were carried out in the presence of a great excess of the second component of the reaction. Hence, all rate constants here are the first-order rate constants, and the rate constant k_2^i involves the concentration of a solvent and is efficient. In the literature dealing with the nucleophilic addition to carbocations, the first-order rate constants are usually used in the study of the reactions with a solvent or in the mixtures of solvents (see [3, 4, 7]). As follows from Fig. 2, the ratio of the concentrations

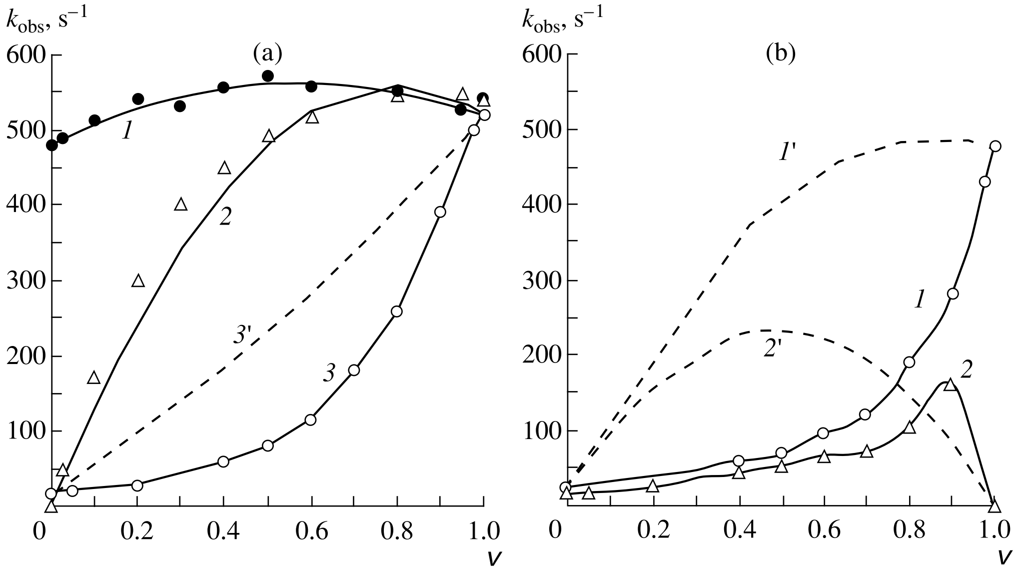


Fig. 1. The rate constant of the carbocation decay k_{obs} as a function of the solvent composition R'OH + R''OH (the first is the solvent, the volume fraction of which (v) is given on the abscissa): (v) (*1*) MeOH + *n*-PrOH, (*2*) MeOH + *i*-PrOH, (*3*) and (*3*') MeOH + H_2O; (*1*) and (*1*') H_2O + *n*-PrOH, (*2*) and (*2*') H_2O + *i*-PrOH. The dashed curves are calculated using Eqs. (4) and (6) with experimental values of α, β, and k_{obs} in pure solvents.

of the adducts formed in the binary mixtures depends linearly on the ratio of the concentrations of the mixture components, that is, Eq. (1) adequately describes the observed dependence of the product composition on the composition of the solvent. The values of α for the mixtures of alcohols and water calculated from these plots are given in the table.

According to the scheme suggested, the lifetime of the carbocation is mainly defined by the rate constant of proton transfer (k_2) to the alcohol or water molecule. It is qualitatively clear from Scheme 3 why the addition of *i*-PrOH to water or MeOH accelerates the carbocation decay. This becomes possible because the rate constant of proton transfer to the solvent (k_2) is higher for *i*-PrOH than for water and MeOH [13].

The concentration of components in the mixture is defined by the expression $[R^iOH] = [R^iOH]_0 v^i$ where $[R^iOH]_0$ is the concentration of the *i*th component in a pure solvent and v^i is the volume fraction of this component in the mixture $v^i = V^i/V$ (V^i is the volume of the *i*th component in the mixture and V is the total volume of the mixture). Therefore, in the processing of the experimental dependences of k_{obs} on the composition of the mixture, the equilibrium constants and the rate constants were used in the form $K^i_{1,\,\text{mix}} = K^i_1 v^i$ and $k^i_{\text{mix}} = k^i v^i$. Since we only dealt in this work with binary mixtures, $v' = v$ and $v'' = 1 - v$. Assuming that the concentrations of the transient cations **B**' and **B**'' are quasi-stationary and that k_2 is independent of **B**, which means that this rate constant is mainly determined by the proton affinity of a solvent, the reasonably simple equation for the observed rate constants can be derived for the two limiting cases. When $k^i_{-1} \ll k^i_2$, after designating $k'_1/k''_1 = \alpha$ and $k'_2/k''_2 = \beta$, the following expression for k_{obs} dependent on the mixture composition is derived:

$$k_{obs} = k''_1 k''_2((\alpha-1)(\beta-1)v^2 + (\alpha+\beta-2)v + 1)/(k'_2 v + k''_2(1-v)). \qquad (2)$$

The ratio of the observed rate constants of the carbocation decay in pure solvents can be derived from Eq. (2) at $v = 1$ and $v = 0$:

$$k'_{obs}/k''_{obs} = \alpha, \qquad (3)$$

that is, the composition of products is consistent with the observed rate constants.

For relatively stable carbocations (k'_{-1}, $k''_{-1} \gg k'_2$, k''_2) using the notation $K'_1/K''_1 = \alpha$ and the same notation for β, the following expression for k_{obs} as a function of the mixture composition can be derived:

$$k_{obs} = K''_1 k''_2((\alpha-1)(\beta-1)v^2 + (\alpha+\beta-2)v + 1), \qquad (4)$$

and then the ratio of the observed rate constants in pure solvents will be defined by the expression

$$k'_{obs}/k''_{obs} = \alpha\beta, \qquad (5)$$

that is, in this case the selectivity is not equal to the ratio of the rate constants in pure solvents. Since the parameter α for 6-Me-DHQ in the mixtures under study ranges from 0.4 to 2.5 (see table), it is clear that the lifetime of the carbocations for the suggested reaction scheme is defined by the rate constant of proton transfer

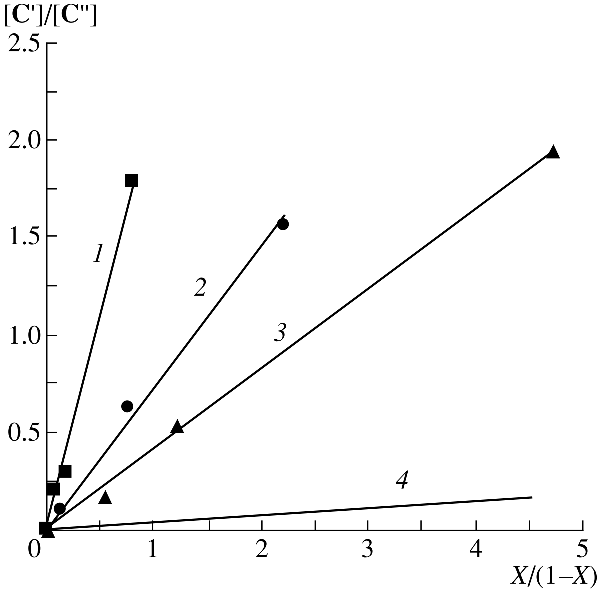


Fig. 2. The product composition for the reaction of the photoaddition of water and alcohols to 6-Me-DHQ as a function of the solvent composition R'OH + R''OH (the first is the solvent, the molar fraction of which is (X): (*1*) H_2O + *n*-PrOH, (*2*) H_2O + MeOH, (*3*) MeOH + *n*-PrOH, and (*4*) the plot for the mixture H_2O + MeOH, calculated on the assumption that $\alpha = k'_{obs}/k''_{obs}$.

(k_2) to the alcohol or water molecule. The values of the parameter β obtained using the experimental values of k'_{obs}, k''_{obs} and α for the mixture under study correlate well with the proton affinity of alcohols and water [13].

For the mixtures with *i*-PrOH, the reaction scheme is simplified, because in this case the formation of only one intermediate **B** with subsequent proton transfer to the two components of the mixture should be considered. The corresponding expression for the observed rate constant of the carbocation decay in the mixture (*i*-PrOH = R'OH) has the form

$$k_{obs} = K_1''k_2''((1-\beta)(1-\nu)^2 + \beta(1-\nu)). \qquad (6)$$

The parameter β for the *i*-PrOH–MeOH mixture was calculated by fitting the dependence of k_{obs} on the solvent composition (Fig. 1a, curve *2*) according to Eq. (6) to the experimental data. For the aqueous mixtures, this approximation was impossible. This problem will be discussed in detail below. Therefore, this parameter for the aqueous solutions was estimated by the combination of the values of β for the *i*-PrOH–MeOH and H_2O–MeOH mixtures.

Scheme 2 is not original. It was suggested by Bunnett [14] for the reactions of olefins with acids in aqueous media and almost always is used when the reactions of carbocations with water and alcohols are discussed (see [7]). However, this scheme has never been used for reactions similar to those studied in this work, because the selectivity of the solvent addition in the mixtures [7] and the rate constants of the carbocation decay measured directly in the last decade [3, 4] did not conflict with one other. This is because the cations studied in [3, 4, 7] have lifetimes on a picosecond time scale and are thus short-lived. In this case, the product composition should be consistent with the observed rate constants (Eq. (3)). Moreover, the assumption of the consistency in the rate constants of nucleophilic addition and product composition has been used to estimate one of the rate constants when the other is known [2, 3, 7]. Unlike [7, 14], reaction (2) in the present work in Schemes 2 and 3 is considered irreversible, because in the photolysis of DHQ the addition of a solvent is quantitative and the backward reaction can be neglected.

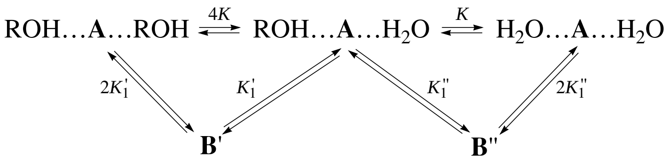
Equations (4) and (6) adequately describe the plots of k_{obs} vs. the solvent composition for the mixtures of alcohols (Fig. 1a, curves *1*, *2*). The values of α and β calculated by fitting the experimental curves *1* and *2* (Fig. 1a) to Eqs. (4) and (6), respectively, using the experimental values of k_{obs} in pure solvents agree with those calculated using Eqs. (1) and (5) within 20%.

Another situation is in water–alcohol solutions. In this case, the values of k_{obs} obtained in the mixtures are less than those calculated from Eqs. (4) and (6) (compare Fig. 1a, curves *3* and *3*' and Fig. 1b, curves *1*, *2* and *1*', *2*'). The least deviations are observed for MeOH, for which the calculated and experimental values of k_{obs} coincide at high concentrations of the alcohol. In the case of the mixtures with EtOH, *n*-PrOH, and *i*-PrOH, the calculated plots have upward convexity ($\alpha < 1, \beta > 1$), and the experimental ones have downward convexity. The discrepancy is not associated with the assumptions made when deriving Eqs. (4)–(6), because these assumptions do not change the parameters α and β and thus cannot change the shape of the curve, but can only change the value of the calculated rate constant.

The consideration of the dependence of the rate constant on the solvent polarity in the form $\log k_{obs} \sim (1 - 1/\varepsilon)$ [15] gives in this case a correction to k_{obs} less than 5% in the solvent of the lower polarity and hence cannot change the shape of the plot. This is consistent with the theoretical concept [15] and the experimental data [7] that the rate constants for the reactions of ions with molecules depend weakly on the solvent polarity. Since the experimental values of k_{obs} correspond to those calculated at higher concentrations of water, the discrepancy is caused by the preferential solvation of the carbocations with water in water–alcohol solutions. This problem has long been widely discussed in the literature (see, for example, [15] and references therein). As follows from theory, in the mixed solvents, ions are preferentially solvated by the component with the highest permittivity, therefore, in the water–alcohol mixtures, carbocations are preferentially solvated by water. In the mixtures of alcohols, the differences in the permittivity are lower and hence these effects are not as pronounced.

It is worth noting that, as stated by Ingold in [16], “provided sufficient water is present for the purpose, the first formed carbenium ion is solvated by a shell of fixed composition so that the rates at which the ion covalently unites with one of the solvating water molecules is independent of the composition of the bulk of the medium.” Although this reasoning dealt with water–acetone mixtures, it can also be applied to water–alcohol mixtures. The weak dependence of the first-order rate constant for the decay of carbocations generated in the photolysis of triarylacetonitriles on the concentration of water in the mixture with acetone observed in [5] was also accounted for by the formation of an aqueous solvate shell. In [7], an increase in the bimolecular rate constant for the reaction of the carbocation and water was observed with a decrease in the concentration of water. In fact, this is the same effect, because the bimolecular rate constant between the particles in the solvate shell is uncertain, because the use of the bulk concentration of the reacting solvent is incorrect in this case.

Several models were suggested to take into account the preferential solvation with water in the nucleophilic combination reaction of a solvent with a carbocation [15]. The simplest model considers the solvation as a sequence of equilibria with the replacement of components in the solvate shell taking into account that there are two components. Within the framework of this model, the formation of the intermediate cations **B**' and **B**'' can be represented by Scheme 4.



Scheme 4.

The composition of products for Scheme 4 also linearly depends on the solvent composition, but the selectivity is defined by the expression $\alpha = K_1'/2KK_1''$, i.e., the factor 2*K* connected with the preferential hydration of the carbocation appears. The comparison of the values of α for the MeOH–*n*-PrOH, MeOH–H_2O, and H_2O–*n*-PrOH mixtures (see table) allows an estimation of the ratio of *K* for the mixtures of methanol and propanol with water. Our data indicate that the hydration of the carbocation in the case of MeOH is lower by a factor of 1.5 than that for propanol. The quantitative treatment of even this simplified scheme is complicated, but this scheme allows us to explain qualitatively the observed regularities in the variation of k_{obs} depending on the solvent composition. A comparison of the data in Figs. 1a (curve *3*) and 1b (curves *1* and *2*) shows that these curves almost coincide up to $v = 0.2$, i.e., the reaction proceeds in the aqueous shell, and a slight increase in k_{obs} is caused by the participation of alcohol from the outer sphere or the bulk solution in step (2). Furthermore, a faster increase in k_{obs} is observed for MeOH indicating that methanol molecules appear in the closest solvate shell. In the case of *n*-PrOH and *i*-PrOH, the k_{obs} constants are close up to $v = 0.4$ with a parallel twofold increase in its value. Then, the plots for *n*-PrOH and *i*-PrOH diverge due to the involvement of *n*-PrOH in step (1) in which *i*-PrOH does not participate.

Thus, in this work, the rate constants for the decay of the carbocations generated in the photolysis of 2,2,4,6-tetramethyl-1,2-dihydroquinoline in water and alcohols are measured. An inconsistency of the product composition in the mixed solvents to the rate constants was found and it was shown that this contradiction can be reconciled assuming that the reaction occurs via two successive steps: the reversible addition of alcohol or water to the carbocation with a subsequent proton transfer to the solvent. The relative reactivity of the alcohols in these steps is estimated. The effect of the preferential solvation of the carbocations with water was shown in the water–alcohol mixture.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 00-03-32190 and 02-03-06489).

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