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Reactivity of the carbocation generated in the photolysis of 1,2,2,4,6-pentamethyl-1,2-dihydroquinoline toward azide ion

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The reaction of the azide ion with the carbocation generated in the photolysis of 1,2,2,4,6-pentamethyl-1,2-dihydroquinoline in methanol was studied by pulse (conventional and laser) and steady-state photolysis techniques. The adduct of the azide ion was characterized by ^{1}H NMR spectrum. Experimental results were interpreted taking into account a competition between the addition of methanol and azide ion to the carbocation. The rate constants for the reaction of the azide ion with the carbocation (k_{Az}) were measured at 2—48 °C in a wide range of $[N_3^-]_0$ concentrations from $2 \cdot 10^{-7}$ to 0.1 mol L^{-1} at different ionic strengths (μ) of the solution. The resulting k_{Az} values are more than an order of magnitude lower than those for diffusional-controlled reactions and vary from $3.2 \cdot 10^8$ (μ = 0) to $4.5 \cdot 10^6$ L mol^{-1} s^{-1} (μ = 0.8 mol L^{-1}) in the presence of NaClO$_4$ (18 °C). The activation energy of addition of the azide ion to the carbocation is 21 kJ mol^{-1}, which is by 12 kJ mol^{-1} lower than the activation energy of the reaction of the carbocation with methanol. The features of the reaction under study are discussed from the viewpoint of the structures of carbocations generated in the photolysis of dihydroquinolines.

Key words: photoaddition, 1,2-dihydroquinolines, carbenium ions, reactivity, conventional and laser pulse photolysis, molecular and ionic nucleophiles, azide ion, ^{1}H NMR spectroscopy.

Carbenium ions (carbocations) are being of interest for more than a century as active intermediates in many organic reactions and metabolic processes in living organisms.[1—7] Carbocations were deeply studied in the presence of superacids.[1] However, problems of the reactivity of cationic intermediates toward nucleophilic reagents, namely, strongly nucleophilic solvents or ionic nucleophiles, remain virtually unsolved. The reactivity toward nucleophiles was measured by direct methods for both stabilized carbocations (stop-flow technique)[2,8] and less stable carbocations (pulse photolysis).[5,6] However, the measurement of selectivity, *i.e.*, ratio of rate constants,[7,9] using competitive reactions remains to be the main method to date. In this method, a cationic intermediate reacts with two nucleophiles to form different products. The absolute rate constants are determined under the assumption that one of the competing nucleophilic reagents reacts with the diffusionally controlled rate constant.[7] The azide ion is one of the most active nucleophiles and is usually used as a reference. In this case, the azide ion is accepted to react with carbocations with a diffusionally controlled rate constant of $5 \cdot 10^9$ L mol^{-1} s^{-1}.[3,7] The development of experimental methods providing measurements of lifetimes of intermediate species down to picoseconds made it possible to study the formation of carbocations and determine relative rate constants of their decay using strong nucleophiles as "clocks" and also to measure absolute values of decay rate constants.[2,3,10,11] As shown for triaryl- and diarylmethyl cations, the assumption that the azide ion reacts with the diffusionally controlled rate constant is valid for carbocations reacting with the nucleophilic solvent (H$_2$O) with the k_s rate constant exceeding 10^5 s^{-1}. In the case of more stable carbocations, the reaction with azide needs activation.[10]

It has recently been shown[12—16] that the photolysis of different derivatives of 2,2,4-trimethyl-1,2-dihydroquinoline (DHQ) in water and methanol produces adducts of the solvent at the double bond of the heterocycle (Scheme 1). The reaction proceeds through the formation of cationic intermediates, which can be observed already 10 ns after the exciting flash in the case of tertiary DHQ (1,2,2,4,6-pentamethyl-1,2-dihydroquinoline (**1**)).

The carbocations from DHQ in alcohols and water are characterized by lifetimes in the millisecond time scale and absorption spectra in the visible region (λ_{max} 480—500 nm) and, hence, can be observed by conventional pulse photolysis technique.[14—16] These intermediates are relatively stable due to resonance stabilization of the carbocation and steric hindrance for adduct formation (see Scheme 1). The carbocations from DHQ are convenient objects for studying reactions of carbocations due to stability and easiness of their generation and observation.

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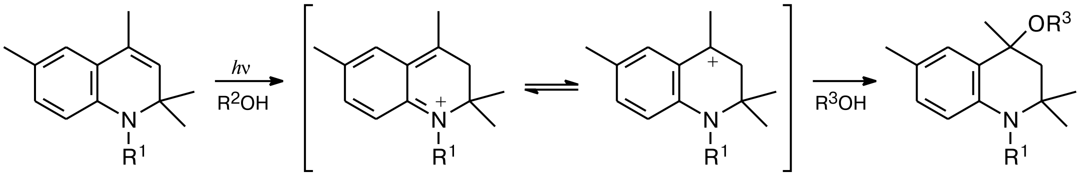
Scheme 1



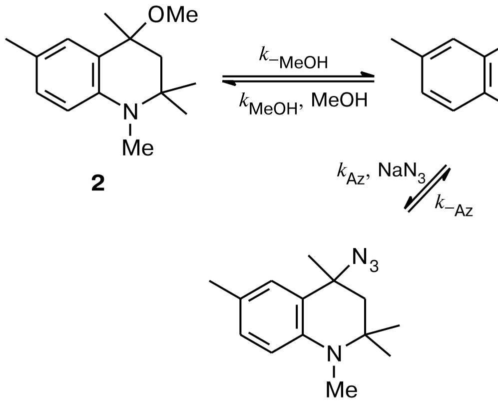
R^1 = H, Me; R^2 = H, Me; R^3 = H, Me, Et, Pr

In this work, the reactivity of carbocations generated from compound **1** toward the azide ion was studied by conventional, laser, and preparative steady-state photolysis.

Results and Discussion

Based on the data of conventional, laser, and steady-state photolysis, we can present the reactions of the carbocations photogenerated from **1** in methanol in the presence of $\mathrm{NaN_3}$ by Scheme 2, where k_{MeOH} is the first-order rate constant of the reaction of the carbocation with the solvent, k_{Az} is the bimolecular rate constant of the reaction of the carbocation with $\mathrm{N_3}^-$, and $k_{-\mathrm{MeOH}}$ and $k_{-\mathrm{Az}}$ are the first-order rate constants of decomposition of adducts **2** and **3**, respectively.

Scheme 2



2

3

The scheme proposed is commonly accepted for the reactions of carbocations with nucleophiles.[3] The data of steady-state preparative photolysis show that the reactions of the carbocation with azide and with MeOH are reversible. The ratio of the yields of the methoxy adduct (**2**) and the adduct with azide (**3**) is virtually independent of the azide concentration, when it increases fivefold from 0.01 to 0.05 mol L^{-1}, and is equal to 1 : 4. The constant composition of a mixture of the adducts is determined by the procedure of their isolation using solvent distillation (see Experimental) and corresponds to the constant concentration of a saturated solution of $\mathrm{NaN_3}$ in methanol $[\mathrm{NaN_3}]_{\mathrm{sat}} \approx 0.2$ mol L^{-1}

$$[\mathbf{2}]/[\mathbf{3}] = K_{\mathrm{MeOH}}/K_{\mathrm{Az}}[\mathrm{NaN_3}]_{\mathrm{sat}}, \qquad (1)$$

where $K_{\mathrm{MeOH}} = k_{\mathrm{MeOH}}/k_{-\mathrm{MeOH}}$ and $K_{\mathrm{Az}} = k_{\mathrm{Az}}/k_{-\mathrm{Az}}$. The estimation from the experimental data on steady-state photolysis gives $K_{\mathrm{MeOH}}/K_{\mathrm{Az}} \approx 0.05$ mol L^{-1}.

However, reversibility of the reactions with the azide ion and methanol is observed in the macroscopic time scale and has virtually no effect on the kinetic data obtained by the pulse technique. This implies that the lifetime of the less stable adduct with azide in methanol is ≥100 ms. In experiments on conventional pulse photolysis of **1** in methanol in the presence of $\mathrm{NaN_3}$ taken in different concentrations, the decay of the absorbance in the region of cation absorption fits well an exponential function. The plot of the apparent pseudo-first-order rate constant $k_{\mathrm{app}} = k_{\mathrm{MeOH}} + k_{\mathrm{Az}}[\mathrm{NaN_3}]_0$ *vs.* $[\mathrm{NaN_3}]_0$ is presented in Fig. 1. For the concentrations used ($[\mathrm{NaN_3}]_0 < 6 \cdot 10^{-6}$ mol L^{-1}), this plot is linear, and k_{app} at $[\mathrm{NaN_3}]_0 = 0$ corresponds to k_{MeOH}. The $k_{\mathrm{Az}}{}^{\mathrm{eff}}$ values calculated from the slopes of the plots of k_{app} *vs.* $[\mathrm{NaN_3}]_0$ at different temperatures are presented in Table 1. Measurements by conventional pulse photolysis become difficult with the further increase in $[\mathrm{NaN_3}]$ and, hence, laser photolysis with a resolution time of 8 ns was used.

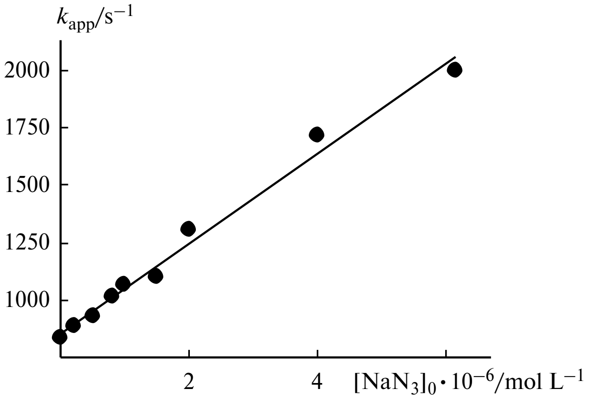


Fig. 1. Apparent rate constant of decay (k_{app}) of the carbocation generated in the conventional pulse photolysis of **1** in methanol *vs.* $[\mathrm{NaN_3}]_0$; 24 °C.

Table 1. Rate constants of the reactions of the carbocation generated from DHQ **1** with methanol (k_{MeOH}) and N_3^- ion (k_{Az}) obtained in experiments on conventional pulse photolysis

T/°C	k_{MeOH}/s^{-1}	$k_{Az} \cdot 10^8$/L mol^{-1} s^{-1}
13	530±50	1.1±0.1
18	680±70	1.4±0.1
24	910±90	1.8±0.2
29	1200±100	2.2±0.2
36	1600±100	2.5±0.3

In this case, two regions of [NaN_3] are observed and manifest different regularities of decay of the carbocation generated from **1** upon laser photolysis in MeOH in the presence of N_3^- (Fig. 2). At $[N_3^-]_0 < 2 \cdot 10^{-4}$ mol L^{-1}, the curves consist of two parts: at first a faster decay is observed, and then the carbocation decays with a rate close to that of its decay in the absence of N_3^-. This feature is most pronounced for curve *3*. The character of the kinetic curves is explained by the competition of the reactions of the carbocation with MeOH and N_3^- at the deficit of the latter. The initial region of the kinetic curve (corresponding to a higher rate of the process) corresponds to both the reactions with N_3^- and MeOH. Then, after N_3^- is consumed, the reaction occurs only with MeOH.

At $[N_3^-]_0 \geq 2 \cdot 10^{-4}$ mol L^{-1}, the decay of the carbocation involves N_3^- and occurs until the carbocation is almost completely consumed (see Fig. 2, curves *4*—*7*). In this case, under the condition that the initial concentration of the carbocation $[\mathbf{C}]_0 \ll [N_3^-]_0$, the carbocation should decay in a reaction of the pseudo-first order with the apparent rate constant, which depends linearly on $[N_3^-]_0$ with the slope equal to k_{Az}.

In fact, at $[N_3^-]_0 > 2 \cdot 10^{-4}$ mol L^{-1}, the carbocation decay obeys a first-order law. However, the plot of k_{app} *vs.* $[NaN_3]_0$ is nonlinear (Fig. 3, *a*). Since in these experiments $[N_3^-]_0$ varied in a wide range from $1.8 \cdot 10^{-4}$ to 0.1 mol L^{-1}, we assume that the nonlinearity was caused by the salt effect.[17] Indeed, at a constant concentration of the salt added [NaN_3] + [$NaClO_4$] = 0.8 mol L^{-1}, the plot of k_{app} *vs.* $[NaN_3]_0$ becomes linear at $[NaN_3]_0 \geq 5 \cdot 10^{-3}$ mol L^{-1} (Fig. 3, *b*).

Table 2. Rate constants of carbocation quenching by the N_3^- ion (k_{Az}) in experiments on laser photolysis at different initial concentrations of NaN_3 and for μ = 0.8 mol L^{-1} in the presence of $NaClO_4$ at different temperatures (2—48 °C)

$[NaN_3]_0$/mol L^{-1} (μ/mol L^{-1})	$k_{Az} \cdot 10^6$/L mol^{-1} s^{-1}		
	2 °C	18 °C	48 °C
$1.85 \cdot 10^{-4}$	125±18	200±30	500±75
$5.54 \cdot 10^{-4}$	126±18	250±40	490±70
$3.07 \cdot 10^{-3}$	100±15	170±25	280±40
$6.15 \cdot 10^{-3}$	—	170±25	—
$9.22 \cdot 10^{-3}$	70±10	130±20	180±30
$3.07 \cdot 10^{-2}$	40±6	75±10	120±20
$7.38 \cdot 10^{-2}$	30±5	60±9	90±15
0.11	—	50±8	—
(0.8)	2.8±0.3	4.5±0.5	9.8±1.0
(0)	150±25	320±40	630±90

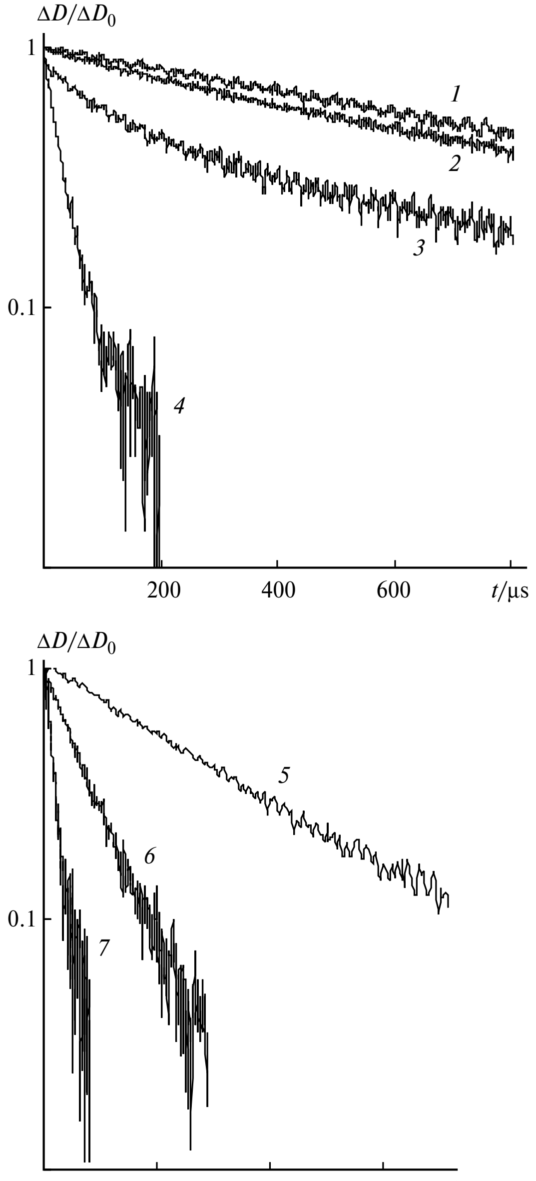


Fig. 2. Time changes in the absorbance (D) at λ = 490 nm corresponding to the absorption maximum of the carbocation generated in the laser photolysis of **1** in methanol in the absence of additives (*1*) and in the presence of the azide ion at $[N_3^-]_0$ = $1.85 \cdot 10^{-5}$ (*2*), $5.5 \cdot 10^{-5}$ (*3*), $1.85 \cdot 10^{-4}$ (*4*), $5.5 \cdot 10^{-4}$ (*5*), $3.0 \cdot 10^{-3}$ (*6*), and $3.0 \cdot 10^{-2}$ mol L^{-1} (*7*); 18 °C; the ordinate is logarithmic.

The k_{Az} values (Table 2) were calculated for both cases: in the absence and presence of $NaClO_4$. In the absence of $NaClO_4$, we assumed that $k_{Az}[N_3^-] = k_{app}$ at $[NaN_3] > 2 \cdot 10^{-4}$ mol L^{-1}. As follows from the data in Table 2,

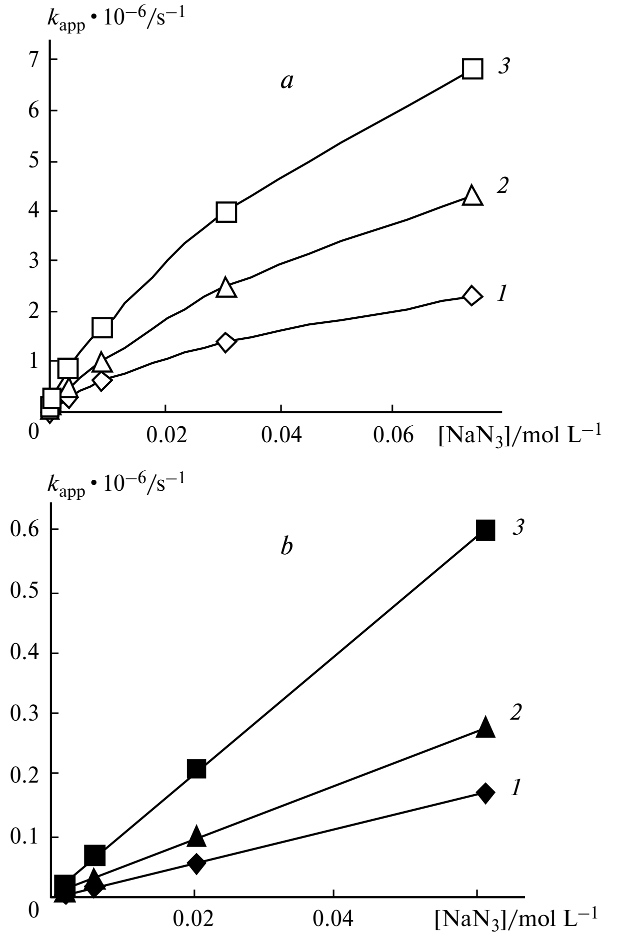


Fig. 3. Apparent rate constant of decay of the carbocation (k_{app}) *vs.* $[NaN_3]_0$ in the absence of added salt (*a*) and in the presence of $NaClO_4$ (μ = 0.8 mol L^{-1}) (*b*) at T = 2 (*1*), 18 (*2*), and 48 °C (*3*); solvent is MeOH.

the k_{Az} values increase with an increase in $[NaN_3]$ from $1.8 \cdot 10^{-4}$ to $5 \cdot 10^{-4}$ mol L^{-1}. This effect is caused by purely kinetic factors related to comparable concentrations of the carbocation and N_3^- (see below). The further increase in the salt concentration decreases k_{Az}. The k_{Az} values, thus calculated and obtained in the presence of $NaClO_4$, at different ionic strengths (μ) are presented in Fig. 4 (in the $\ln k_{Az}$—$\mu^{0.5}$ coordinates).[17] Two regions of ionic strength values are clearly seen. At $\mu \geq 1 \cdot 10^{-2}$ mol L^{-1}, these dependences are satisfactorily approximated by straight lines, whose slopes are virtually temperature-independent. At $\mu < 1 \cdot 10^{-2}$ mol L^{-1}, k_{Az} increases more sharply with a decrease in the salt concentration (see Fig. 4). The $k_{Az}{}^0$ values equal to the rate constant of the reaction of the carbocation with the azide ion at μ = 0 mol L^{-1}, which were calculated by extrapolation of these curves to μ = 0, are presented in Table 2. The complicated character of the plot of $\ln k_{Az}$ *vs.* $\mu^{0.5}$ is, most likely, a consequence of both nonspecific and specific salt effects.[17]

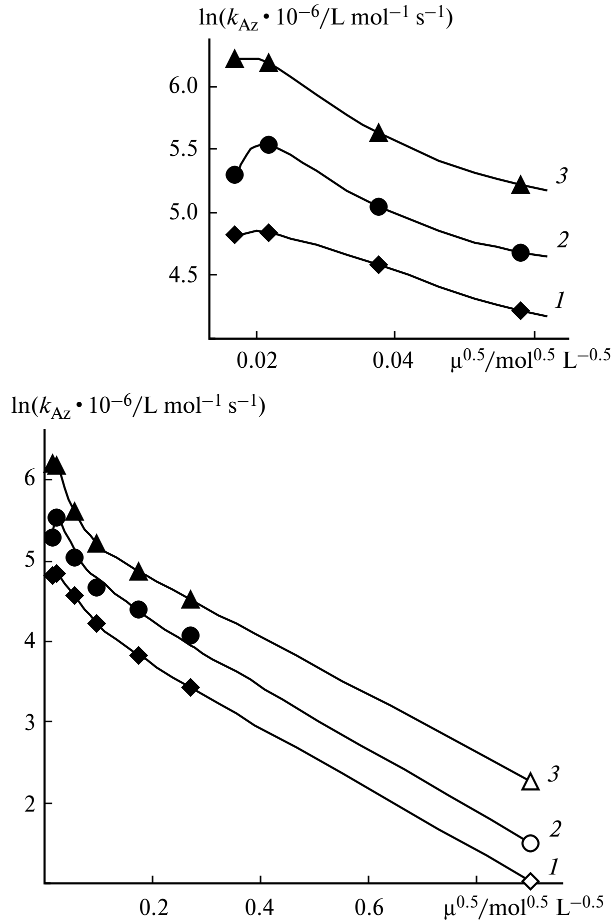


Fig. 4. Plots of $\ln k_{Az}$ *vs.* $\mu^{0.5}$ in the absence of $NaClO_4$ (dark points) and in the presence of $NaClO_4$ at μ = 0.8 mol L^{-1} (light points) at T = 2 (*1*), 18 (*2*), and 48 °C (*3*).

It should be noted that the $k_{Az}{}^0$ value thus calculated is higher than k_{Az} obtained in conventional pulse photolysis experiments at low azide concentrations (see Table 1) when the salt effect can be neglected. Naturally, the question arises: is this discrepancy a result of an experimental error of measurements or caused by other factors? This problem is important, especially taking into account that in the experiments on conventional pulse photolysis the carbocation concentration ($[\mathbf{C}]_0$) is ~$4 \cdot 10^{-6}$ mol L^{-1} and the concentration of N_3^- is varied within $2 \cdot 10^{-7}$—$6 \cdot 10^{-6}$ mol L^{-1}, *i.e.*, the concentrations of the reagents are comparable. Under these conditions, the kinetics of carbocation decay should not be described by the pseudo-first order equation. It is known that a system of differential equations for the rate of a process consisting of two parallel reactions, one of which is a reaction of the first order and another reaction has the second order, is solved analytically. However, the solution is inconvenient for experimental checking. Therefore, the system of differential equations corresponding to this scheme was solved numerically for the rate constant values determined experimentally and concentrations close to those used in experiments on conventional pulse photolysis: $k_{\text{MeOH}} = 800\ \text{s}^{-1}$, $k_{\text{Az}} = 2 \cdot 10^8\ \text{L mol}^{-1}\ \text{s}^{-1}$, $[\mathbf{C}]_0 = 4 \cdot 10^{-6}\ \text{mol L}^{-1}$, $[\text{NaN}_3]_0 = (0, 0.2, 0.5, 1.0, 5.0, 10, \text{and } 50) \cdot 10^{-6}\ \text{mol L}^{-1}$. The results of numerical integration show that at these concentrations the resulting calculated kinetic curves of carbocation decay with the correlation coefficient $R^2 = 1$—0.9998 are described by exponential laws. The linear dependence of the effective pseudo-first-order rate constant k^{eff}, which is determined from these curves, on $[\text{NaN}_3]_0$ is well fulfilled ($R^2 = 0.998$). However, the rate constant $k_{\text{Az}}{}^{\text{eff}} = 1.3 \cdot 10^8$ L mol^{-1} s^{-1}, which was calculated from the slope of this straight line at $[\text{N}_3{}^-]_0 \le 5 \cdot 10^{-6}\ \text{mol L}^{-1}$, is lower than the k_{Az} value used in calculations. Thus, underestimated values of the rate constants are experimentally obtained, in fact, in this case.

The numerical calculations at $[\mathbf{C}]_0 = 1 \cdot 10^{-4}\ \text{mol L}^{-1}$ and the same values of rate constants showed that they are completely adequate to the results obtained in experiments on laser photolysis. At $[\text{NaN}_3]_0 < 2 \cdot 10^{-4}\ \text{mol L}^{-1}$, the kinetic curves are not linearized in the semilogarithmic coordinates. At $[\text{NaN}_3]_0 \approx 2 \cdot 10^{-4}\ \text{mol L}^{-1}$, up to 90% of the carbocation decay in the first-order reaction. In the concentration region $2 \cdot 10^{-4} < [\text{NaN}_3]_0 < 1 \cdot 10^{-3}\ \text{mol L}^{-1}$, $k_{\text{Az}} = k_{\text{app}}/[\text{NaN}_3]_0$ increases from $1.2 \cdot 10^8$ to $1.82 \cdot 10^8\ \text{L mol}^{-1}\ \text{s}^{-1}$. At $[\text{NaN}_3]_0 > 1 \cdot 10^{-3}$ mol L^{-1}, the k_{Az} value, calculated from the slope of the straight line of k_{app} *vs.* $[\text{NaN}_3]_0$ with an accuracy exceeding 95%, corresponds to a value of $2 \cdot 10^8\ \text{L mol}^{-1}\ \text{s}^{-1}$ used in numerical calculations.

The k_{Az} values obtained make it possible to estimate the ratio of decomposition rate constants for adducts **2** and **3** using the ratio of equilibrium constants measured in experiments on steady-state photolysis taking into account the $K_{\text{Az}}/K_{\text{MeOH}}$ ratio at $[\text{NaN}_3]_{\text{sat}} \approx 0.2\ \text{mol L}^{-1}$. At this $[\text{NaN}_3]$ value, $k_{\text{Az}} \approx 3 \cdot 10^7\ \text{L mol}^{-1}\ \text{s}^{-1}$ and, after insertion of k_{Az} and k_{MeOH} into the ratio of equilibrium constants, we have that at room temperature $k_{-\text{MeOH}}/k_{-\text{Az}} \approx 5 \cdot 10^{-4}$, *i.e.*, the lifetime of adduct **2** in MeOH is three orders of magnitude higher than that of adduct **3**. The adduct of the carbocation under study with the azide ion is unstable, as well as the hydroxy adduct of compound **1**. At the same time, the adducts with alcohols and the hydroxy adduct of the respective *sec*-DHQ (2,2,4,6-tetramethyl-1,2-dihydroquinoline[18]) are stable.

The activation energy of the reaction is $E_a(\text{N}_3{}^-) = 21 \pm 2\ \text{kJ mol}^{-1}$, which was determined from the temperature dependences of $k_{\text{Az}}{}^0$ and k_{Az} at $\mu = 0.8\ \text{mol L}^{-1}$. Its value depends weakly on the ionic strength of the solution, although the rate constants differ by two orders of magnitude. The $E_a(\text{N}_3{}^-)$ value obtained in laser photolysis experiments is close to the activation energy measured by conventional pulse photolysis technique.

The carbocation under study is relatively stable, and the rate constant of its decay in MeOH changes from 300 to 3000 s^{-1} in a temperature interval of 0—50 °C. According to the accepted classification,[10] the reaction of this carbocation with the azide ion should occur with a rate constant lower than those for diffusion-controlled reactions. The experimental results presented in this work confirm this prediction. A sufficiently high activation energy is an additional evidence for the activation control of the reaction. It should be noted that the activation energy of the reaction of the carbocation under study with $\text{N}_3{}^-$ is much lower than those of the reactions with MeOH and H_2O ($E_a(\text{MeOH}) = 32\ \text{kJ mol}^{-1}$ and $E_a(\text{H}_2\text{O}) = 50\ \text{kJ mol}^{-1}$).[16] Unfortunately, published data on temperature dependences of rate constants of reactions of carbocations with nucleophiles are scarce. These data were obtained by indirect methods in experiments on solvolysis from analysis of reaction products and determine the difference in the activation energies of the reactions of carbocations with a solvent and $\text{N}_3{}^-$. It has been found[19] for the hydrolysis of di-*p*-tolylmethyl chloride that the activation energy of the reaction of the corresponding carbocation with water is by 16.8 kJ mol^{-1} lower than that of the reaction of the same carbocation with $\text{N}_3{}^-$. The difference in activation energies was determined[20] for the carbocation formed in solvolysis of camphene hydrochloride: $E_a(\text{N}_3{}^-) - E_a(\text{MeOH}) = 8.4$—$12.6\ \text{kJ mol}^{-1}$. Thus, although the reaction of the carbocation with the azide ion is faster than the reaction with a nucleophilic solvent, its activation energy is higher in these cases. It is assumed[21] that for carbocations in the solvate shell of a nucleophilic solvent the reaction with the solvent requires a lower activation than the reaction with an anion, which needs an additional energy to be delivered through this solvate shell. The higher activation energy of the reaction of the carbocation from **1** with MeOH and water compared to that with $\text{N}_3{}^-$ is a consequence of a complex two-step interaction of the carbocations with the solvent. This is especially pronounced for the carbocations from DHQ due to the specific features of their structure: resonance stabilization with predominant localization of a positive charge on the N atom and steric hindrance for adduct formation.[22] Unlike the reactions with anions, which occur in one step, the reaction of the carbocations with molecular nucleophiles occurs in two steps. The addition of a molecular nucleophile is followed by the second step related to the elimination of a proton from the oxonium cation formed. The higher activation energy of the reaction with molecular nucleophiles than that with ionic nucleophiles in the case of the carbocation from **1** indicates that proton elimination occurs with a substantial activation energy in the case of the cations under study. This problem will be considered in more detail elsewhere.

Experimental

1,2,2,4,6-Pentamethyl-1,2-dihydroquinoline (1) was synthesized according to a previously published procedure[23] by the reaction of 2,2,4,6-tetramethyl-1,2-dihydroquinoline with MeI, b.p. 150—152 °C (12 Torr). ^{1}H NMR (DMSO-d_6), δ: 1.21 (s, 6 H); 1.89 (d, 3 H, J = 1.1 Hz); 2.16, 2.68 (both s, 3 H each); 5.33 (d, 1 H, J = 1.1 Hz); 6.40 (d, 1 H, J_m = 8.25 Hz); 6.81 (d, 1 H, J_o = 2.2 Hz); 6.85 (dd, 1 H, J_m = 8.25 Hz, J_o = 2.2 Hz).

Sodium azide NaN_3 (DIFCO, USA) and $NaClO_4$ (reagent grade, Russia) were used as received. Methanol for spectroscopy (Merck) was preliminarily boiled to remove water and acid traces and distilled over $Mg(MeO)_2$. Solutions of **1** containing NaN_3 in a specified concentration were prepared by the addition of the calculated amount of a solution of NaN_3 in MeOH (0.1 mol L^{-1}).

Absorption spectra and the kinetics of formation and decay of short-lived intermediate species were measured using a pulse photolysis technique with a time resolution of 10 μs.[24] Samples were irradiated in 10-cm quartz cells using a Xe lamp with a flash energy of 150 J. Changes in absorbance were detected using a system consisting of a Xe lamp (75 W), a ZMP-3 monochromator, and a photomultiplier connected with an S9-8 digital storage oscilloscope. To excite the long-wave band of **1** (λ_{max} = 350 nm in MeOH), the light was passed through a UFS-5 filter (the transmission region is 300—400 nm with the maximum transmission at 365 nm).

An experimental laser photolysis setup has been described in detail elsewhere.[25] The setup includes a PRA LN-1000 nitrogen laser (337 nm) as an excitation source and a kinetic spectrophotometer (resolution time 8 ns) with an averaging system consisting of a Biomation 6500 oscillograph connected with a personal computer.

Steady-state photolysis of **1** (10 mg of the substance in 20 mL of a solution of NaN_3 (0.01—0.05 mol L^{-1}) in MeOH, [**1**] ≈ $2.5 \cdot 10^{-3}$ mol L^{-1}) was carried out along with magnetic stirring in a glass (Pyrex) flask. Irradiation was performed with the unfiltered light from a DRSh-1000 mercury lamp (the light filter was the glass of the flask with transmission at $\lambda > 290$ nm), exciting the long-wavelength absorption band (λ_{max}(MeOH) = 355 nm) at ~20 °C. The reaction was monitored by changes in the UV spectra in the region of long-wavelength absorption of the starting compound **1** (λ_{max} = 355 nm) and adducts **2** and **3** (λ_{max} = 305—310 nm) with a Shimadzu UV-1601 PC spectrometer in quartz cells with an optical path length of 0.2 cm with periodical sampling. After the end of the reaction, the solvent was distilled off *in vacuo* at ~20 °C, and the residue was dissolved in DMSO-d_6 and analyzed by ^{1}H NMR with a Bruker WM-250 spectrometer. The ^{1}H NMR spectrum was recorded without separation of products, because **3** is unstable. The spectrum of the product represented a superposition of the known spectrum of compound **2** [13] (15—20 mol.%) and the spectrum of **3** (85—80 mol.%).

4-Azide-1,2,2,4,6-pentamethyl-1,2,3,4-tetrahydroquinoline (3). ^{1}H NMR (DMSO-d_6), δ: 1.18, 1.21, 1.41 (all s, 3 H each); 1.94, 2.22 (both d, 1 H each, J = 14.1 Hz); 2.20, 2.70 (both s, 3 H each); 6.58 (d, 1 H, J_m = 8.3 Hz); 6.98 (dd, 1 H, J_m = 8.3 Hz, J_o = 2.1 Hz); 7.10 (d, 1 H, J_m = 2.1 Hz).

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References

1. G. A. Olah, *J. Org. Chem.*, 2001, **66**, 5943.
2. C. D. Ritchie, *Acc. Chem. Res.*, 1972, **5**, 348.
3. J. P. Richard, T. L. Amyes, and M. M. Toteva, *Acc. Chem. Res.*, 2001, **34**, 981.
4. R. A. McClelland, *Tetrahedron*, 1996, **52**, 6823.
5. V. B. Ivanov, V. L. Ivanov. and M. G. Kuzmin, *Zh. Org. Khim.*, 1972, **8**, 621 [*J. Org. Chem. USSR*, 1972, **8** (Engl. Transl.)].
6. V. B. Ivanov, V. L. Ivanov, and M. G. Kuzmin, *Mol. Photochem.*, 1974, **6**, 125.
7. J. P. Richard, M. E. Rothenberg, and W. P. Jencks, *J. Am. Chem. Soc.*, 1984, **106**, 1361.
8. C. D. Ritchie, *Can. J. Chem.*, 1986, **64**, 2239.
9. R. Ta-Shma and Z. Rappoport, *J. Am. Chem. Soc.*, 1983, **105**, 6082.
10. R. A. McClelland, V. M. Kanagasabapathy, N. Banait, and S. Steenken, *J. Am. Chem. Soc.*, 1991, **113**, 1009.
11. R. A. McClelland, F. L. Cozens, S. Steenken, T. L. Amyes, and J. P. Richard, *J. Chem. Soc.*, *Perkin Trans. 2*, 1993, 1717.
12. T. D. Nekipelova, L. N. Kurkovskaya, I. I. Levina, N. A. Klyuev, and V. A. Kuzmin, *Izv. Akad. Nauk*, *Ser. Khim.*, 1999, 2072 [*Russ. Chem. Bull.*, 1999, **48**, 2049 (Engl. Transl.)].
13. T. D. Nekipelova, L. N. Kurkovskaya, I. I. Levina, V. S. Shishkov, and V. A. Kuzmin, *Izv. Akad. Nauk*, *Ser. Khim.*, 2001, 647 [*Russ. Chem. Bull.*, *Int. Ed.*, 2001, **50**, 673].
14. T. D. Nekipelova, *Photochem. Photobiol. Sci.*, 2002, **1**, 204.
15. T. D. Nekipelova, Yu. A. Ivanov, E. N. Khodot, and V. S. Shishkov, *Kinet. Katal.*, 2002, **43**, 333 [*Kinet. Catal.*, 2002, **43**, 303 (Engl. Transl.)].
16. T. D. Nekipelova, V. S. Shishkov, and V. A. Kuzmin, *Khim. Vys. Energ.*, 2002, **36**, 225 [*High Energy Chem.*, 2002, **36**, 183 (Engl. Transl.)].
17. J. E. Gordon, *The Organic Chemistry of Electrolyte Solutions*, Wiley, New York, 1975.
18. T. D. Nekipelova, L. N. Kurkovskaya, and I. I. Levina, *Izv. Akad. Nauk*, *Ser. Khim.*, 2002, 1899 [*Russ. Chem. Bull.*, *Int. Ed.*, 2002, **51**, 2055].
19. A. R. Hawdon, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1952, 2499.
20. C. A. Bunton, T. W. Del Pesco, A. M. Dunlop, and K.-H. Yang, *J. Org. Chem.*, 1971, **36**, 887.
21. C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornel University Press, Ithaca, 1969, Ch. VII.
22. T. D. Nekipelova, I. I. Levina, and V. S. Shishkov, *Kinet. Katal.*, 2004, **45**, 28 [*Kinet. Catal.*, 2004, **45** (Engl. Transl.)].
23. E. Knoevenagel, *Ber.*, 1921, **54**, 1722.
24. Yu. E. Borisevich, A. S. Tatikolov, and V. A. Kuzmin, *Khim. Vys. Energ.*, 1978, **12**, 474 [*High Energy Chem.*, 1978, **12** (Engl. Transl.)].
25. P. P. Levin and V. A. Kuzmin, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1986, 464 [*Bull. Acad. Sci. USSR*, *Div. Chem. Sci.*, 1986, **35**, 430 (Engl. Transl.)].

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