Kinetics and Mechanism of Unimolecular Heterolysis of Cage-Like Compounds: XIX.* Effect of the Nucleofuge Nature on the Activation Parameters of Heterolysis of 1-Halo-1-methylcyclohexanes in Cyclohexane. Heterolysis Rate Ratio in Aprotic and Protic Solvents

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Abstract—Heterolysis of 1-bromo-1-methylcyclohexane in cyclohexane (E1 reaction) involves solvation of the transition state ($\Delta S^{\neq} = -81$ J mol^{-1} K^{-1}), while heterolysis of 1-chloro-1-methylcyclohexane is characterized by desolvation of the transition state ($\Delta S^{\neq} = 92$ J mol^{-1} K^{-1}). The probability for the formation of transition state (interaction between cationoid intermediate and solvent cavity) increases in the first case due to enhanced stability of the solvated intermediate, and in the second, due to reduction in its size. The bromide/chloride heterolysis rate ratio decreases as the ionizing power of aprotic solvent decreases and that of protic solvent increases.

The rate of unimolecular heterolysis (S$_N$1, E1, solvolysis) of alkyl halides in the nucleofuge series I > Br > Cl usually decreases by 2 to 3 orders of magnitude [2, 3] due to increase in the carbon–halogen bond energy: 240, 270, and 325 kJ/mol, respectively. The rate of these reactions is determined by heterolytic dissociation of the covalent bond, which includes consecutive formation of three types of ion pairs: contact, loose, and solvent-separated [4–6]. The driving force of heterolysis in a protic medium is electrophilic assistance by the solvent, which becomes stronger as the solvent electrophilicity (acidity) and nucleofuge electronegativity rise [2, 4, 7, 8]. Increase in the acidity of a protic solvent could level the nucleofuge effect on the reaction rate and even invert the reactivity series. For example, the ratio of the rates of solvolysis of 1-adamantyl iodide (1-AdI) and 1-adamantyl bromide (1-AdBr) in EtOH at 25°C is equal to 4, in 2,2,2-tri-fluoroethanol, to 1, and in (CF$_3$)$_2$CHOH, to 0.4 [9, 10]. Analogous inversion of the reactivity was observed in the solvolysis of various secondary (Ph$_2$CHX, i-PrX) and primary alkyl halides (RCH$_2$X, 1-halomethylnaphthalenes, allyl halides) [11, 12].

The nucleofuge effect on the rate of heterolysis in aprotic solvents weakens as the ionizing power of the medium decreases [13, 14]. For example, the rate of heterolysis of 1-chloro-1-methylcyclohexane (**I**) in propylene carbonate is lower by two orders of magnitude than the rate of heterolysis of 1-bromo-1-methylcyclohexane (**II**), while in cyclohexane, the rates of both reactions are similar [15, 16].

We performed correlation analysis of solvation effects and found that the rate of heterolysis of compounds **I** and **II** depends on the solvent polarity (which is a function of its dielectric constant ε), electrophilicity (E), and cohesion energy density (δ^2).

$$\log k_{\mathbf{I}} = -(11.0 \pm 0.2) + (2.07 \pm 0.72)(\varepsilon - 1)/(2\varepsilon + 1)$$
$$+ (0.0345 \pm 0.0100)E + (0.00210 \pm 0.00100)\delta^2; \quad (1)$$
$$R = 0.954, \ S = 0.20, \ N = 20;$$

$$\log k_{\mathbf{II}} = -(12.1 \pm 0.3) + (8.08 \pm 1.21)(\varepsilon - 1)/(2\varepsilon + 1)$$
$$+ (0.0541 \pm 0.0170)E + (0.00215 \pm 0.00100)\delta^2; \quad (2)$$
$$R = 0.969, \ S = 0.34, \ N = 20.$$

The polarity and electrophilicity of aprotic solvents affect the rate of heterolysis of bromide **II** more strongly (by factors of 3.9 and 1.6, respectively) than

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* For communication XVIII, see [1].

the rate of heterolysis of chloride **I**. The reason is likely to be higher polarizability of the C–Br bond, which facilitates electrostatic solvation of bromide.

In cyclohexane ($E = 0$), the difference between compounds **I** and **II** is determined only by the solvent polarity ($\varepsilon = 2.02$), while the effects of cohesion energy density ($\delta^2 = 281$ kJ mol^{-1} l^{-1}) are almost similar. Calculation using Eqs. (1) and (2) gives $\log k_{\mathbf{I}} = -9.99$ and $\log k_{\mathbf{II}} = -9.87$; these values satisfactorily coincide with those found experimentally [14–16]: $\log k_{\mathbf{I}} = -9.88$, $\log k_{\mathbf{II}} = -9.56$. The fact that the free term in Eq. (3) is considerably smaller than in Eq. (2) is also responsible for the close rates of heterolysis of chloride **I** and bromide **II** in cyclohexane. Substituting the parameters for vacuum ($\varepsilon = 1$, $E = 0$, $\delta^2 = 0$) into Eqs. (2) and (3) leads to $\log k_{\mathbf{I}} = -11.0$, $\log k_{\mathbf{II}} = -12.1$, i.e., compound **I** appears to be more reactive than **II** by an order of magnitude.

Presumably, the rate-determining stage in the gas phase is the formation of contact ion pair. The most stable conformation of 1-halo-1-methylcyclohexanes is *chair* with the halogen atom occupying axial position [17]. The higher reactivity of chloride **I** compared to bromide **II** may be rationalized in terms of the greater electronegativity of the nucleofuge: the formation of cyclic transition state like **A** via interaction between the axial halogen atom and axial hydrogen atom in the 3-position is more energetically favorable for X = Cl.

If the dehydrohalogenation according to the *E*1 mechanism does not involve cyclic transition state like **A**, bromides in the gas phase react at a higher rate than chlorides; however, the bromide/chloride heterolysis rate ratio strongly falls down as the ionizing power of aprotic solvent decreases [5, 15, 16]. For example, 1-chloro-1-methylcyclopentane (**III**) in propylene carbonate reacts more slowly than does 1-bromo-1-methylcyclopentane (**IV**) by 3 orders of magnitude ($\log k_{\mathbf{III}} = -6.57$, $\log k_{\mathbf{IV}} = -3.51$), whereas the corresponding difference in going to cyclohexane is only one order of magnitude ($\log k_{\mathbf{III}} = -9.87$, $\log k_{\mathbf{IV}} = -8.60$).

We obtained the following correlations for the heterolysis of chloride **III** and bromide **IV** in aprotic solvents [15]:

$$\log k_{\mathbf{III}} = -11.8 + 7.30(\varepsilon - 1)/(2\varepsilon + 1) + 0.0718E; \quad (3)$$
$$R = 0.957, \, S = 0.30, \, N = 21;$$

$$\log k_{\mathbf{IV}} = -11.2 + 11.5(\varepsilon - 1)/(2\varepsilon + 1) + 0.0912E; \quad (4)$$
$$R = 0.971, \, S = 0.26, \, N = 20.$$

Thus the reactivities of five-membered substrates become close as the ionizing power of solvent de-

creases; the reason is that the effects of the solvent polarity and electrophilicity on the rate of heterolysis of the bromide are stronger by factors of 1.6 and 1.3, respectively, as compared to the corresponding chloride.

Heterolysis of five-membered halogen-containing substrates is likely to involve a linear transition state, for formation of a six-membered cyclic activated complex is impossible for steric reasons, and the probability for formation of a four-membered complex is low [18]. In fact, gas-phase heterolysis of *t*-BuCl and *t*-BuBr occurs through a linear transition state like **B** [2, 5], though the formation of four-membered cyclic transition state **C** is often postulated without any substantiation [19, 20]. The formation of a linear activated complex is supported by the fact that the entropy of activation in the dehydrohalogenation of *tert*-butyl halides in the gas phase is close to zero ($\Delta S^{\neq} \approx 0$) [2]. The formation of a four-membered cyclic transition state could be accompanied by reduction in the entropy by 100–150 J mol^{-1} K^{-1} [21, 22].

A **B** **C**
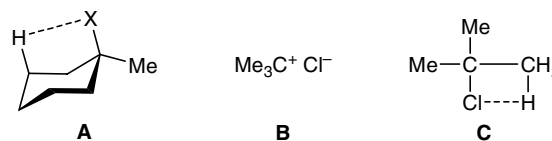
Decrease in the solvent ionizing power also makes the rates of heterolysis of *t*-BuCl and *t*-BuBr in aprotic media closer, for the effects of the solvent polarity and electrophilicity on the heterolysis of *t*-BuBr are stronger by factors of 1.5 and 1.1, respectively, than on the heterolysis of *t*-BuCl [5, 23].

In order to get mechanistic explanations of the fact that the rate of heterolysis of 1-halo-1-methylcyclohexanes in cyclohexane almost does not depend on the nucleofuge nature, we compared the corresponding entropies and enthalpies of activation. For this purpose, we examined temperature effect on the rates of heterolysis of 1-halo-1-methylcyclohexanes **I** and **II** in cyclohexane. These reactions are very slow: the half-conversion period for chloride **I** at 25°C is about 200 years. Therefore, we used the verdazyl technique [6, 24] which makes it possible to determine within several hours the rate of a reaction with a half-conversion period of about 1000 years.

Kinetic experiments were carried out in the presence of a small amount (~10^{-4} M) of 3,5-bis(4-methoxyphenyl)-1-phenylverdazyl (Vd$^\cdot$) which quickly and quantitatively reacted with the solvent-separated ion
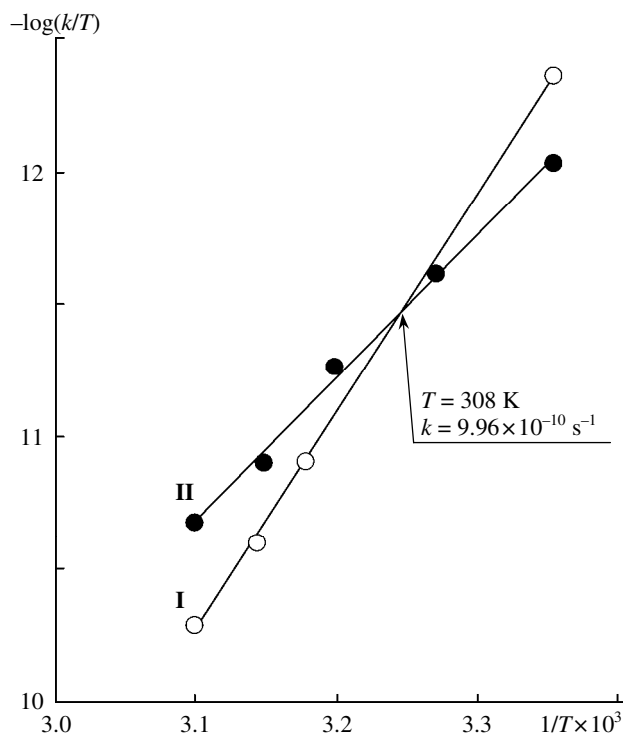
Scheme 1.

X = Cl, Br.
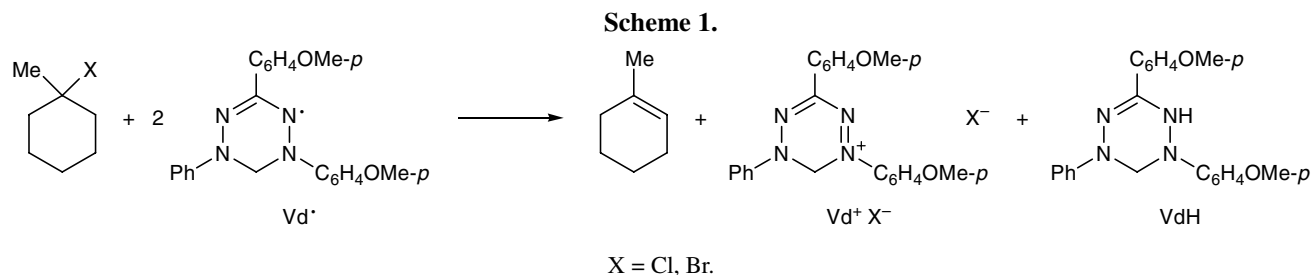
pair derived from the substrate to give the corresponding olefin, verdazylium salt Vd⁺X⁻, and leucoverdazyl VdH (Scheme 1). The reaction rate was measured by spectrophotometry, following decrease in the concentration of Vd˙ (λ_{max} = 740 nm, ε = 3500); it satisfactorily fits first-order kinetic equation (5):

$$v = -\partial[\text{Vd}^{\cdot}]/2\partial\tau = k[\text{RX}]. \qquad (5)$$

The results of experiments carried out at 25°C demonstrated their reliability: k_I = (1.22±0.15)×10⁻¹⁰, k_{II} = (2.72±0.16)×10⁻¹⁰ s⁻¹; these values agree satisfactorily with those determined previously: k_I = 1.32× 10⁻¹⁰, k_{II} = 2.74×10⁻¹⁰ s⁻¹ [15, 16].

Figure 1 shows the dependence log(k/T)—1/T. The activation parameters for the heterolysis of 1-halo-1-methylcyclohexanes **I** and **II** in cyclohexane were thus estimated as follows: $\Delta H_I^{\neq}$ = 157±2 kJ/mol, $\Delta S_I^{\neq}$ = 92±6 J mol⁻¹ K⁻¹, $\Delta G_I^{\neq}$ = 129±4 kJ/mol; $\Delta H_{II}^{\neq}$ = 103±4 kJ/mol, $\Delta S_{II}^{\neq}$ = −81±11 J mol⁻¹ K⁻¹, $\Delta G_{II}^{\neq}$ = 128±7 kJ/mol. Bromide **II** at 25°C is more reactive than chloride **I** by a factor of 2.2; at 35°C, the rates of their heterolysis become similar (k_I = k_{II} = 9.96× 10⁻¹⁰ s⁻¹); and at 49.5°C chloride **I** is more reactive than bromide **II** by a factor of 1.6.

Although the nature of nucleofuge in 1-methyl-cyclohexyl halides **I** and **II** weakly affects the rate of their heterolysis in cyclohexane, the enthalpies and entropies of activation of these reactions differ considerably. This may be rationalized in terms of solvation effects. In the heterolysis of bromide **II** solvation of the transition state ($\Delta S^{\neq}$ < 0) stabilizes cationoid intermediate, and $\Delta H^{\neq}$ decreases. The heterolysis of chloride **I** involves desolvation of the transition state ($\Delta S^{\neq}$ > 0), so that $\Delta H^{\neq}$ sharply increases. As a result of $\Delta H^{\neq}$–$\Delta S^{\neq}$ compensation, the $\Delta G^{\neq}$ values become closer.

Thus the relative rates of heterolysis of compounds differing only by the nucleofuge nature strongly depend on the solvent. In protic solvents, increase of the ionizing power leads to leveling and subsequent inversion of the reactivities of such substrates, for the effect on the less active substrate is stronger (especially, the effect of solvent electrophilicity) [9, 10]. The reason is greater electronegativity of the nucleofuge in less reactive substrate and hence higher sensitivity to electrophilic assistance by the solvent via formation of H-complex RX···HOS. In aprotic solvents, leveling of the substrate reactivities occurs when the ionizing power of the medium decreases; here, the effect (especially of the solvent polarity) is stronger on the more reactive substrate due to greater polarizability of the C–Br bond compared to C–Cl, which favors dipolar solvation. Thus the solvation effects in protic and aprotic solvents are different; therefore, these effects should be analyzed separately for each group of solvents.

Solvent effects on the heterolysis rate ratio of substrates differing only in the nucleofuge nature may

Fig. 1. Temperature dependences of the rate constants for heterolysis of 1-chloro-1-methylcyclohexane (**I**) and 1-bromo-1-methylcyclohexane (**II**) in cyclohexane.

be roughly illustrated by a rhomboid dependence in the $\log k$—E_T coordinates (Fig. 2). Here, the right-hand part of the rhomboid refers to protic solvents, and the left-hand part, to aprotic ones. The bottom sides reflect the effect of solvent ionizing power on the rate of heterolysis of substrates with more electronegative nucleofuge (less reactive substrates), while the upper sides show the effect on the more active substrate containing less electronegative nucleofuge.

The maximal difference in the rates of heterolysis of such substrates is observed in most polar aprotic solvents (e.g., propylene carbonate) and least polar protic solvents (*tert*-butyl alcohol). In these cases, $E_T \approx$ 200 kJ/mol, and the difference in the reaction rates is 2 to 3 orders of magnitude. When the polarity of an aprotic solvent decreases to $E_T \approx$ 130 kJ/mol (cyclohexane) or the polarity of a protic solvent increases to $E_T \approx$ 270 kJ/mol (hexafluoropropan-2-ol), the difference in the rates of heterolysis becomes smaller since the rate of heterolysis of more reactive substrate depends to a stronger extent on E_T of aprotic solvent and the rate of heterolysis of less reactive substrate depends to a stronger extent on E_T of protic solvent. In the limiting cases, the rates of heterolysis of the substrates under study may coincide or be inverted.

Formation of an ion pair in the course of heterolysis is accompanied by structuring of the solvent around that intermediate (electrostriction); as a result, $\Delta S^{\neq}$ falls down. Electrostriction in protic solvents leads to destructurization thus raising $\Delta S^{\neq}$. The entropy of activation in aprotic solvents is always less than zero, and its value characterizes difference in the solvation of the initial and transition states. Taking into account that coordination of one unidentate ligand is accompanied by loss of ~45 J mol^{-1} K^{-1} [25], we presume that two solvent molecules are additionally involved in the formation of transition state in the heterolysis of bromide **II**. By contrast, the formation of transition state from chloride **I** involves desolvation of two solvent molecules.

According to the transition state theory [6, 26], solvation of transition state is an equilibrium process, i.e., solvate shells of the initial and transition states should have similar structures. In this case, the entropy of activation should not change, $\Delta S^{\neq} = 0$. This assumption is based on the postulate implying that the time necessary for transition state formation (~10^{-13} s [27]) is insufficient for reorganization of solvate shell, which requires 10^{-10}–10^{-11} s [28]. In our case, $\Delta S^{\neq}$ values are considerably different from zero. Therefore, we should
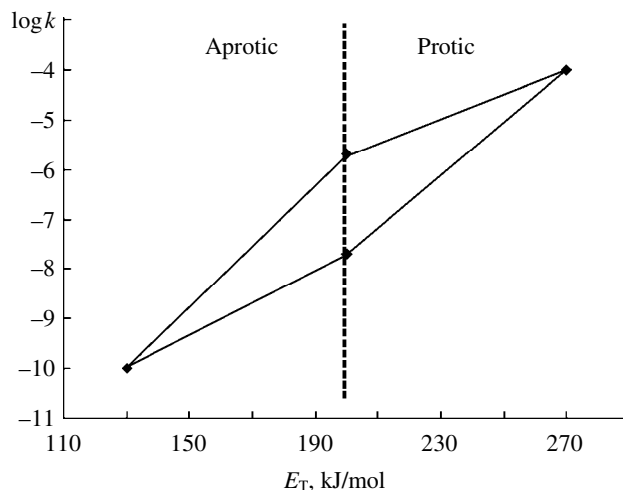

Fig. 2. Plots of the rate of heterolysis of substrates differing only by the nucleofuge nature versus ionizing power of solvent E_T.

speak about nonequilibrium solvation [26] which is related to orientational polarization [29]; the latter is characterized by a sufficiently high rate (~10^{-16} s), so that it capable of affecting transition state formation. However, orientational polarization could not affect $\Delta S^{\neq}$. Change of $\Delta S^{\neq}$ requires essential reorganization of the initial state solvate shell. It is reasonable to presume that the initial state includes several solvates and that only some of them could reach transition state [30]. It follows that in the heterolysis of bromide **II** only the most solvated substrate molecules reach the transition state, while in the heterolysis of chloride **I**, the least solvated. Why?

Transition state in the heterolysis is formed via interaction between the substrate contact ion pair and solvent cavity. Cavities continuously appear and disappear in solution as a result of density fluctuations, and they move as "waves through the medium" [6, 31]. The probability for transition state formation depends on the lifetime of cationoid intermediate and the size of its solvate shell, for the ion separation process in a contact ion pair requires a small energy [4, 5]. Ingold estimated that energy at 17 kJ/mol in benzene [32]. According to the Coulomb law, extension of interionic distance from 0.25 nm (the distance assumed for a contact ion pair) to 1 nm (the distance assumed for a solvent-separated ion pair) in a vacuum requires an energy of ~20 kJ/mol. However, in going to polar solvents ($\varepsilon \geq 30$) this value decreases to <1 kJ/mol. More advanced calculations [33] and experimental methods [34, 35] give a value of 3–8 kJ/mol for the energy of ion separation in a contact ion pair. From the

above stated it follows that the energy of ion separation is not the main factor determining the limiting stage and that the latter is determined by the frequency of encounters of a contact ion pair with solvent cavities having a required size. The heterolysis of bromide **II** is favored by increase of the contact ion pair lifetime due to additional solvation, while the heterolysis of less solvated chloride **I** is favored by reduction of the size of solvated contact ion pair.

We can conclude that nonpolar aprotic solvents could exert specific solvation effects capable of strongly changing the relative reactivity of compounds, which is typically observed in polar solvents. These effects include that of solvent cavity.

EXPERIMENTAL

1-Chloro-1-methylcyclohexane (**I**) and 1-bromo-1-methylcyclohexane (**II**) were synthesized by reaction of 1-methylcyclohexan-1-ol with PCl_3 and PBr_3, respectively. Excess PCl_3 or PBr_3, was added dropwise under stirring and cooling to a solution of 1-methyl-cyclohexan-1-ol in anhydrous pentane, the mixture was stirred for 1 h at room temperature, the pentane solution was washed with cold water and dried over Na_2SO_4 and K_2CO_3, the solvent was distilled off, and the residue was subjected to fractional distillation under reduced pressure. Yield of **I** 50–52%, bp 56°C (14 mm), $n_D^{20} = 1.4866$; published data [36]: bp 83–84°C (100 mm), $n_D^{20} = 1.4868$. Compound **II**: bp 42°C (15 mm), $n_D^{20} = 1.4578$; published data [36, 37]: bp 78–79°C (38 mm), $n_D^{20} = 1.4578$. Compounds **I** and **II** were stored in a desiccator over $CaCl_2$ at ~4°C. The substrates were distilled before each series of kinetic experiments. 3,5-Bis(4-methoxyphenyl)-1-phenylverdazyl was synthesized and purified as described in [38]. Cyclohexane was washed in succession with concentrated sulfuric acid, water, and aqueous sodium carbonate, dried in succession over sodium sulfate and metallic sodium, and distilled over metallic sodium.

Kinetic measurements were performed using an SF-26 spectrophotometer in cells maintained at a constant temperature. Some experimental data obtained at 25°C were characterized by a relatively large dispersion, and it was difficult to define the linear dependence [Vd˙]—τ with a required accuracy. Therefore, after measuring the reaction rate, the reaction solution was left to stand overnight at 25°C, and the concentration of Vd˙ was determined over a period of several hours. In such a way, a required accuracy was attained. The substrate concentration in kinetic experiments was 0.19 to 0.74 M, the concentration of verdazyl indicator was $(1–2)\times10^{-4}$ M, and the substrate conversion was $(1.4–28)\times10^{-4}$ %. The error in the determination of the rate constants was ±10%. Given below are temperature (°C) and $k\times10^9$ (s^{-1}): 1-chloro-1-methylcyclohexane (**I**): 25.0, 0.122; 41.5, 3.84; 45.0, 7.97; 49.5, 11.2; 1-bromo-1-methylcyclohexane (**II**): 25.0, 0.272; 32.5, 0.742; 39.5, 1.70; 44.5, 3.98; 49.5, 6.80.

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