

# Kinetics and Mechanism of Unimolecular Heterolysis of Framework Compounds: XVII.\* Solvation Effects in Dehydrobromination of *tert*-Butyl Bromide, 1-Bromo-1-Methylcyclohexane, and 2-Bromo-2-methyladamantane in Dipolar Aprotic Solvents

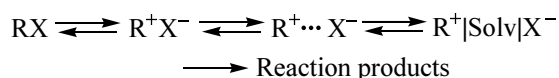
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Received October, 4 2004

**Abstract**—Dehydrobromination rate of *tert*-butyl bromide, 1-bromo-1-methylcyclohexane, and 2-bromo-2-methyladamantane grows with increasing polarity and dipole moment of solvents. No correlation was found between rate constants of the process and electrophilicity or ionizing power of the solvents. The observed solvation effects are due mainly to dispersion interactions.

The dehydrobromination of *tert*-butyl bromide (**I**) [2], 1-bromo-1-methylcyclohexane (**II**) [3], and 2-bromo-2-methyladamantane (**III**) [4] follows the *E1* mechanism. According to the modern data [5, 6] the unimolecular heterolysis (*E1*,  $S_N1$ , solvolysis) proceeds through successive formation of three types ion pairs: contact, space-separated, and solvent-separated.



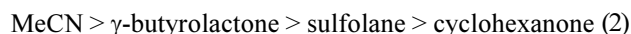
In the limiting stage the contact ion pair interacts with a cavity in the solvent which results from the fluctuation of the liquid density [7] (the cavities amount to ~10% of the liquid volume [8]). Thus a space-separated ion pair is formed that quickly transforms into the solvent-separated ion pair which in its turn rapidly affords the reaction products. The rate of these reactions is described by the first order kinetic equation (1).

$$v = k[\text{RBr}] \quad (1)$$

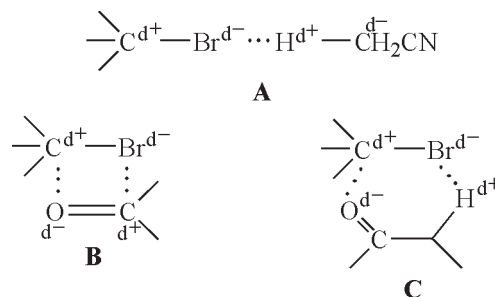
One of the previous communications from this series [9] contains data on the heterolysis kinetics of 2-bromo-2-phenyladamantane (**IV**) in MeCN,  $\gamma$ -butyrolactone, sulfolane, and cyclohexanone ( $S_N1$  reaction). In the mentioned solvent series the reaction rate decreased by three orders of magnitude because of diminishing of the ionizing power ( $E_T$ [8]) and electrophilicity of the solvent. No correlation with the solvent polarity was observed.

\* For communication XXII, see [1].

The rate of the unimolecular heterolysis is commonly governed by the polarity and electrophilicity of solvents [5, 6]. These parameters determine also the ionizing power of the solvents. Therefore the decrease in the heterolysis rate of bromide **IV** in the solvent series (2) is caused mainly by the reduced electrophilic assistance from the solvent, and in going to the cyclohexanone additionally by the diminished polarity of the medium (the polarity of the other three solvents does not significantly differ).



It is presumed [9] that the electrophilic assistance to the heterolysis of bromide **IV** originates mainly from orientation and dipole-dipole interactions: in MeCN forms a linear quadrupole **A** involving a hydrogen bond, in the  $\gamma$ -butyrolactone arises a cyclic quadrupole **B**, and in sulfolane possessing the highest value of the Gutman acceptor number *AN* [8] the molecule of the substrate coordinates with a solvent molecule providing a charge-transfer complex. In the least polar cyclohexanone the



nucleofuge solvation in the transition state occurs by forming a cyclic solvate **C**.

These conceptions are based on comparison of the activation parameters of the reaction. The quadrupole formation is accompanied by a decrease in  $\Delta S^\ddagger$  value by  $\sim 80 \text{ J mol}^{-1} \text{ K}^{-1}$  [9, 10], and a coordination of a single monodentate ligand result in a loss of  $\sim 45 \text{ J mol}^{-1} \text{ K}^{-1}$  [11, 12]. The formation of solvate **C** is in agreement with a sharp decrease both in the enthalpy and entropy of activation for the reaction in cyclohexanone [9].

In continuation of the research on the nature of the solvation effects in the unimolecular heterolysis we planned to study the influence of the substrate structure on these effects in dipolar aprotic solvents. To this end we compared the values of  $\log k$ ,  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  for the heterolysis of bromides **I–III** in the solvents of the series (2).

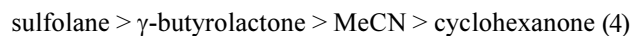
Kinetic parameters were published on heterolysis of bromide **I** in MeCN [2] and  $\gamma$ -butyrolactone [13], of bromide **II** in MeCN [3], and of bromide **III** in MeCN [4] and  $\gamma$ -butyrolactone [13]. With the use of verdazyl method [5, 9] we studied the kinetics of dehydrobromination of bromides **I–III** in sulfolane and cyclohexanone, and also of bromide **II** in  $\gamma$ -butyrolactone at various temperatures. As an internal indicator we used in the kinetic experiments 1,3,5-triphenylverdazyl (Vd<sup>+</sup>) that quickly and quantitatively reacted with the solvent-separated ion pair of the substrate to give olefins **V–VII**, verdazyl salt (Vd<sup>+</sup>Br<sup>-</sup>), and leuoverdazyl (VdH). The reaction proceeds in keeping with a stoichiometric equation [5].

The reaction rate was measured by the decrease in the verdazyl concentration Vd<sup>+</sup>. The rate is satisfactorily described with the kinetic equation (3).

$$v = -d[\text{Vd}^+]/2d\tau = k[\text{RBr}] \quad (3)$$

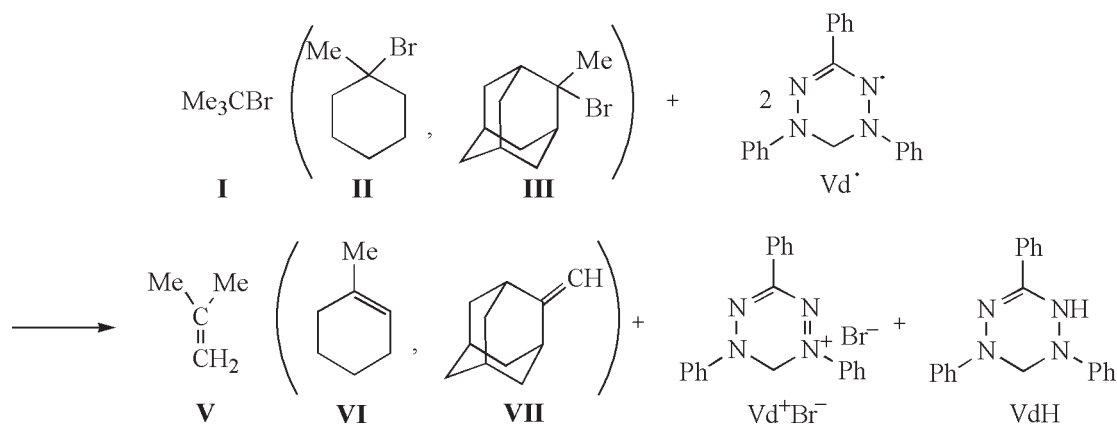
Kinetic parameters of the reactions of the substrates under study and some data on the solvents are presented

in a table. The reaction rate decreased in the series of solvents (4):



In this series the polarity of solvents (dielectric constant  $\epsilon$ ) decreases, and electrophilicity ( $E$ ) and ionizing power of the solvents ( $E_T$ ) first grow and then diminish in going to cyclohexanone. As in the case of bromide **IV** heterolysis, the reaction rate is the least in cyclohexanone for all the three substrates under study. However the effects of the first three solvents for substances **I–III** were opposite to those observed for bromide **IV**. In the solvent series sulfolane– $\gamma$ -butyrolactone–MeCN the heterolysis rate of bromide **IV** grew nearly by an order of magnitude, and the heterolysis rate of bromides **I–III** decreased 5.2, 3.0, and 2.2 times respectively. This difference is due to dissimilar sensitivity of the substrates to the electrophilicity and polarity of the solvents. Whereas the electrophilicity has the decisive importance for bromide **IV**, with the other substrates polarity is the most significant.

The observed solvent effect on the heterolysis rate of the four substrates is understandable under assumption that in the heterolysis of bromides **I–III** the solvation originates mainly from the dispersion forces, and the orientation and dipolar interactions that dominate in the heterolysis of bromide **IV** are less important. The prevalence of the dispersion interaction is apparently due to the presence of a methyl group at the  $\alpha$ -carbon hampering the dipolar solvation. The dispersion forces to a great extent depend on the polarizability of the solvent, therefore the dehydrobromination rate of the substrates under study grows with the growing dipolarity (polarity–polarizability,  $\pi^*$  [8]) and the dipole moment ( $\mu$ ) of solvents. Usually the dispersion forces dominate in the



Heterolysis characteristics of bromides **I–III** in dipolar aprotic solvents<sup>a</sup>

| Solvent                 | <b>I</b>       |  |   | <b>II</b>      |  |   |  |  |  |
|-------------------------|----------------|--|---|----------------|--|---|--|--|--|
|                         | $-\log k_{25}$ | $\Delta H^\ddagger$ , kJ mol <sup>-1</sup> | $-\Delta S^\ddagger$ , kJ mol <sup>-1</sup> K <sup>-1</sup> | $-\log k_{25}$ | $\Delta H^\ddagger$ , kJ mol <sup>-1</sup> | $-\Delta S^\ddagger$ , kJ mol <sup>-1</sup> K <sup>-1</sup> |  |  |  |
| Cyclohexanone           | 7.82 (7.82)    | 100 ± 3                                    | 59 ± 8  | 7.10 (7.37)    | 77 ± 3                                     | 122 ± 5   |  |  |  |
| MeCN                    | 5.90 (5.86)    | 82   | 84  | 6.00           | 71 ± 5                                     | 122 ± 14  |  |  |  |
| $\gamma$ -Butyrolactone | 5.62 (5.61)    | 86 ± 5                                     | 65 ± 15   | 5.80 (5.84)    | 68 ± 2                                     | 126 ± 7   |  |  |  |
| Sulfolane               | (5.18)         | 86 ± 3                                     | 54 ± 9  | (5.52)         | 69 ± 4                                     | 119 ± 16  |  |  |  |

| Solvent                 | <b>III</b>     |  |   | $E_T$ , kJ mol <sup>-1</sup> | $E$ , kJ mol <sup>-1</sup> | $\epsilon$ | $\mu$ | $\pi^*$ |
|-------------------------|----------------|--|---|------------------------------|----------------------------|------------|-------|---------|
|                         | $-\log k_{25}$ | $\Delta H^\ddagger$ , kJ mol <sup>-1</sup> | $-\Delta S^\ddagger$ , kJ mol <sup>-1</sup> K <sup>-1</sup> |                              |                            |            |       |         |
| Cyclohexanone           | 6.30 (6.31)    | 100 ± 3                                    | 30 ± 8  | 171                          | 2.1                        | 18.3       | 3.01  | 0.76    |
| MeCN                    | 4.07 (4.06)    | 77 ± 3                                     | 65 ± 8  | 193                          | 21.8                       | 37.5       | 3.44  | 0.75    |
| $\gamma$ -Butyrolactone | 4.03 (4.02)    | 79 ± 4                                     | 57 ± 11   | 186                          | 12.1                       | 39         | 4.12  | 0.87    |
| Sulfolane               | (3.78)         | 43 ± 3                                     | 153 ± 9   | 184                          | 9.6                        | 44         | 4.81  | 0.98    |

<sup>a</sup> The values in parentheses are evaluated from the temperature dependence.

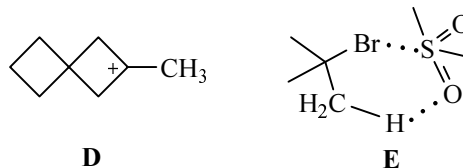
solvents of low polarity, but they may give the main contribution into the interaction of polar molecules with a constant dipole moment [14].

The relative activity of bromides **I–III** strongly depends on the nature of solvent. For instance, in going from bromide **I** to bromide **IV** the heterolysis rate in MeCN grew by ~3 orders of magnitude, in  $\gamma$ -butyrolactone by ~2 orders of magnitude, in sulfolane by ~1 order of magnitude, i.e., the difference decreased with the diminishing electrophilicity of the solvent [15, 16].

The difference in activity of *tert*-butyl and adamantyl substrates is known to decrease with the growing electrophilicity of the solvent. For instance, in the propylene carbonate (*E* 20) *tert*-butyl iodide is by ~4 orders of magnitude more active than 1-adamantyl iodide [2, 17], in 80% aqueous ethanol *tert*-butyl halides are by ~3 orders of magnitude more active than 1-adamantyl halides [2, 15, 18], in 2,2,2-trifluoro-1-ethanol (*E* 81) this difference for chlorides and bromides equals to 20 [5, 15, 18], and in 1,1,1,3,3-hexafluoro-2-propanol (*E* 88) it amounts to ~2 [5, 15, 18]. The changes in relative rates of heterolysis of the *tert*-butyl halides and 1-adamantyl halides is due to the greater sensitivity of the less active adamantyl substrates to the electrophilicity of solvents. Thus in going from propylene carbonate to hexafluoro-2-propanol the heterolysis rate of *tert*-butyl bromide grows by ~4 orders of magnitude, and that of 1-adamantyl bromide by ~8 orders of magnitude.

In our case the adamantyl substrate, bromide **III**, is more active. Its heterolysis rate grows with increasing electrophilicity of the solvent, and the heterolysis rate of bromide **I** decreases. The latter fact results from the decreasing dipolarity and dipole moment in the series of solvents (4) that proves to be decisive for bromide **I**. As we already mentioned, in the heterolysis of bromide **IV** the dipolar solvation led to a linear quadrupole **A**; with bromide **I** this solvation apparently also provided a similar quadrupole (this assumption agreed with the value of  $\Delta S^\ddagger$  in MeCN), but this effect had however a secondary importance.

The heterolysis rate of bromide **II** is nearly the same as that of bromide **I** but in contrast to the latter whose decrease in the heterolysis rate in the solvents series (4) is due to the alterations in both activation parameters, the decrease in the heterolysis rate of bromide **II** is caused by the growth of the  $\Delta H^\ddagger$  value, whereas the  $\Delta S^\ddagger$  values in all solvents are virtually constant and ~2 times less than those of bromide **I**. The special behavior of the activation parameters in the heterolysis of bromide **II** originates apparently from the conformational effects weakly sensitive to the nature of solvent. The cyclohexyl substrate in the ground state exists in the *chair* form, and



the carbocation arising in the transition state has a *twist*-conformation **D** [3, 19] thus governing the spatial requirements to the formation of the transition state.

Under these conditions the reaction rate is determined by the stability of carbocations that grows with the growing dielectric constant of the solvent.

The heterolysis rate of bromide **III** is nearly by two orders of magnitude greater than the reaction rates of bromides **I** and **II**. The values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  in the heterolysis of bromide **III** depend strongly on the solvent character and grow in the series (4). The relatively low  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values in sulfolane may result from the involvement into formation of the transition state of two solvent molecules (hexapole formation) or from reaction via cyclic solvate **E**.

Close values of the heterolysis rate in sulfolane for bromides **III** and **IV** ( $\log k_{25} = -3.78$  and  $-3.87$  respectively) and strong difference in the values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  [for bromide **III**  $43 \text{ kJ mol}^{-1}$  and  $-153 \text{ J mol}^{-1} \text{ K}^{-1}$ , for bromide **IV**  $87 \text{ kJ mol}^{-1}$  and  $-13 \text{ J mol}^{-1} \text{ K}^{-1}$  respectively] confirm the dissimilar nature of the solvation effects in the heterolysis of these substrates.

In cyclohexanone the heterolysis of all substrates is the slowest. Unlike the reaction in sulfolane the values  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  in the heterolysis of bromide **III** are considerably greater than those of bromide **IV** [for bromide **III**  $100 \text{ kJ mol}^{-1}$  and  $-30 \text{ J mol}^{-1} \text{ K}^{-1}$ , for bromide **IV**  $63 \text{ kJ mol}^{-1}$  and  $-151 \text{ J mol}^{-1} \text{ K}^{-1}$  respectively]. These data once more confirm the difference in the solvation effects in the heterolysis of these substrates and also show that in cyclohexanone the decisive role belongs to dispersion interactions.

## EXPERIMENTAL

The substances **I–III** were synthesized and purified as described in [3, 4, 9]. The solvents were purified by procedures from [9]. The kinetic measurements were carried out in a cell of spectrophotometer SF-26 equipped with the temperature control; concentration of substrates **I–III**  $0.03\text{--}0.00$ , of verdazyl indicator  $(0.80\text{--}3.3) \times 10^{-4} \text{ mol l}^{-1}$ ; conversion of substrates in all cases was below 0.01%.

Further are reported: substrate – solvent, temperature ( $^\circ\text{C}$ ),  $k \times 10^6 \text{ (s}^{-1}\text{)}$ .

Bromide **I** – sulfolane: 30.5,  $12.1 \pm 0.9$ ; 35.0,  $22.0 \pm 0.5$ ; 39.0,  $34.8 \pm 0.7$ ; 46.0,  $67.5 \pm 0.1$ ; cyclohexanone: 17.0,  $0.00467 \pm 0.00032$ ; 20.0,  $0.00739 \pm 0.00052$ ; 25.0,  $0.0162 \pm 0.011$ ; 30.0,  $0.0307 \pm 0.0002$ ; 36.0,  $0.0363 \pm 0.0023$ ; 39.5,  $0.0917 \pm 0.0009$ .

20.0,  $0.917 \pm 0.021$ ; 25.0,  $1.56 \pm 0.14$ ; 30.0,  $2.27 \pm 0.07$ ; 35.0,  $3.62 \pm 0.23$ ; sulfolane: 30.0,  $4.60 \pm 0.40$ ; 32.5,  $6.10 \pm 0.20$ ; 34.5,  $8.00 \pm 0.10$ ; 40.5,  $11.3 \pm 1.3$ ; 45.0,  $19.0 \pm 1.0$ ; cyclohexanone: 13.0,  $0.0191 \pm 0.0002$ ; 20.0,  $0.0408 \pm 0.0012$ ; 25.0,  $0.0802 \pm 0.0030$ ; 29.5,  $0.117 \pm 0.008$ ; 35.0,  $0.206 \pm 0.010$ .

Bromide **III** – sulfolane: 30.0,  $234 \pm 12$ ; 32.5,  $279 \pm 15$ ; 35.0,  $324 \pm 8$ ; 39.0,  $423 \pm 20$ ; cyclohexanone: 16.0,  $0.136 \pm 0.007$ ; 20.5,  $0.261 \pm 0.003$ ; 25.0,  $0.601 \pm 0.016$ ; 30.0,  $0.926 \pm 0.012$ ; 36.0,  $2.16 \pm 0.06$ .

The study was carried out under financial support of the Ukrainian State Foundation for Fundamental Research.

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