

Kinetics and Mechanism of Unimolecular Heterolysis of Framework Compounds: XX.* Solvation and Steric Effects in Heterolysis of 2-Halo-2-alkyladamantanes in Sulfolane and Butanol

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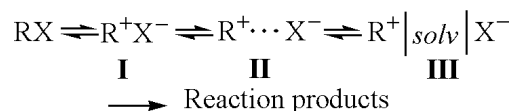
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Received May 3, 2005

Abstract—Heterolysis rate of 2-halo-2-phenyladamantanes in BuOH is 1000 times higher than the heterolysis rate of 2-halo-2-methyladamantanes. The heterolysis rate in sulfolane does not depend on the substituent, but the phenyl group exhibits a negative steric effect.

DOI: 10.1134/S1070428007020066

The rate of unimolecular heterolysis (S_N1 , $E1$, solvolysis) is governed by the ionization of a covalent bond occurring through successive formation of three ion pairs: contact (**I**), space-separated (**II**), and solvent-separated (**III**) [2, 3].



In the limiting stage ion pair **I** interacts with a void in the solvent (the voids constitute approximately 10% of the liquid volume [4]). Thus forms ion pair **II** that rapidly transforms into ion pair **III**, and the latter quickly provides the reaction products.

The rate of these reaction is described by a first order kinetic equation $v = k[\text{RX}]$. The rate is strongly dependent on the polarity of the solvent: For instance, in going from hexane to water the heterolysis rate of *t*-BuCl increased by a factor of 14 orders of magnitude [5]. This is caused by a strong solvation of the polar transition state. The information on the nature and strength of solvation effects can be gained by comparative analysis of the activation parameters in various heterolysis reactions.

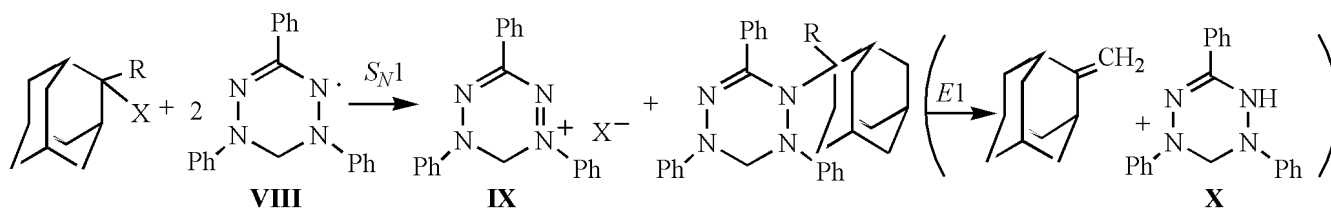
In this respect the entropy of activation is especially interesting, whose magnitude and sign in reactions of

unimolecular heterolysis strongly depends on the solvent nature. The ion pair arising in the heterolysis causes structurization of the solvent around this intermediate (electrostriction effect [6]) thus decreasing the ΔS^\ddagger value. In protic solvents structurized by hydrogen bonds formation the electrostriction damages the structure of the solvent thus increasing the ΔS^\ddagger value. In aprotic solvents the activation entropy is as a rule negative, and its value indicates the additional number of solvent molecules involved in the solvation of the transition state as compared to that of the initial state, and the steric hindrances caused by this solvation. In protic solvents at prevailing electrostriction effect $\Delta S^\ddagger < 0$, and at predominant damaging the solvent structure $\Delta S^\ddagger > 0$ [2].

Steric effects can both decrease and increase the heterolysis rate [7]. For instance, in going from 2-methyl-2-adamantyl tosylate to 2-*tert*-butyl-2-adamantyl tosylate the solvolysis rate in 80% aqueous ethanol became 5 orders of magnitude larger [8]. Similar steric effects should strongly affect the ΔS^\ddagger and ΔH^\ddagger values.

We planned to investigate the solvent effect and the influence of a hydrocarbon substituent in heterolysis of 2-methyl-2-chloro-2-adamantane (**IV**), 2-phenyl-2-chloro-2-adamantane (**V**), 2-bromo-2-methyladamantane (**VI**), and 2-bromo-2-phenyladamantane (**VII**) in sulfolane and BuOH. The data on heterolysis kinetics in sulfolane for bromides **VI** and **VII** are published in [9, 10]. The kinetics of the other reactions we studied by verdazyl method [11]

* For Communication XIX, see [1].



in the temperature range 20–50°C. We used as internal indicator 1,3,5-triphenylverdazyl (**VIII**) that quickly and quantitatively reacted with the solvent-separated ion pair of the substrate giving verdazylum salt **IX** and product of verdazyl alkylation (reaction S_N1) [11]. In the heterolysis of methyl derivatives the alkylation product decomposed in sulfolane into an olefin and leuoverd-azyl **X** (reaction $E1$). In butanol formed verdazylum salt **IX**, solvolysis product, and compound **X**. The reaction proceeded in keeping with the stoichiometric equation.

Irrespective of the heterolysis type (S_N1 , $E1$, solvolysis) one mol of the substrate reacts with two mols of radical **VIII**. The reaction rate was measured spectrophotometrically by consumption of radical **VIII**, and it is fairly described by the first order kinetic equation: $v = -d[\text{VIII}]/2dt = k[\text{RX}]$.

In the table are compiled the $\log k_{25^\circ\text{C}}$ values and activation parameters of heterolysis of halides **IV–VII** in sulfolane and butanol. The ionizing power E_0 of butanol is considerably higher than that of sulfolane (210 and 184 kJ mol⁻¹ respectively), but the heterolysis rates of tertiary chlorides and bromides in these solvents are commonly similar. For instance, the values $\log k_{25^\circ\text{C}}$ for *t*-BuCl are 7.91 and 7.28, and for *t*-BuBr, 5.18 and 5.61

respectively [5, 12]. The higher activity of chlorides in alcohol is usually attributed to the strong electrophilic assistance of the solvent by formation of a strong hydrogen bond with the nucleofuge, and the higher activity of bromides in sulfolane is ascribed to higher polarizability of the C–Br bond facilitating intensive dipolar solvation [13].

In our event the difference in heterolysis rates of halides **IV–VII** in sulfolane and butanol is considerably greater, especially for phenyl derivatives **V** and **VII** that react in BuOH ~ 100 times faster, whereas methyl derivatives **IV** and **VI** are more active in sulfolane. It is known that at replacing a methyl group by a phenyl one, e.g., in going from *t*-BuCl to PhCMe₂Cl, the heterolysis rate in protic and aprotic solvents is 3–4 orders of magnitude higher [5, 14]; therewith the acceleration is caused by a decrease in the ΔH^\ddagger value due to enhanced stability of the carbocation intermediate resulting from the conjugation between the *p*-orbitals of the carbocation and the phenyl group. In heterolysis of halides **IV–VII** these trends are observed only in butanol whereas in sulfolane the heterolysis rate both of chlorides and bromides is virtually insensitive to the nature of the hydrocarbon substituent, and the ΔH^\ddagger values are smaller for the methyl derivatives.

Kinetic parameters of heterolysis of 2-halo-2-methyl- and 2-halo-2-phenyladamantanes **IV–VII** in BuOH and sulfolane

| Substrate | $-\log k_{25^\circ\text{C}}$ | ΔG^\ddagger , kJ mol ⁻¹ | ΔH^\ddagger , kJ mol ⁻¹ | ΔS^\ddagger , J mol ⁻¹ K ⁻¹ |
|------------|------------------------------|--|--|---|
| BuOH | | | | |
| IV | 6.95 | 113 ± 10 | 117 ± 5 | 13 ± 5 |
| V | 3.93 | 95 ± 6 | 101 ± 3 | 17 ± 9 |
| VI | 4.94 | 101 ± 10 | 87.2 ± 5.4 | -47 ± 16 |
| VII | 2.15 | 85 ± 12 | 56.1 ± 6.3 | -98 ± 19 |
| Sulfolane | | | | |
| IV | 6.33 ^a | 109 ± 11 | 89.9 ± 5 | -68 ± 18 |
| V | 6.39 ^a | 109 ± 3 | 104 ± 2 | -18 ± 5 |
| VI | 3.78 ^a | 94.5 ^b | 48.9 ^b | -153 ^b |
| VII | 3.87 ^a | 95 ^b | 93.3 ^b | -13 ^b |

^a Calculated from $\log k$ values obtained at higher temperature. ^b From [9].

These relationships are difficult to understand, the solvation effects only are not enough for their interpretation. The different behavior in butanol and sulfolane apparently originates from various manifestations of steric effects of methyl and phenyl groups in these solvents. The phenyl is considerably more bulky than methyl. Spatial parameters calculated from the average van der Waals radii of these groups are 1.66 and 0.52 respectively [15]. However not only the volume of the phenyl group is important, but also its ability to be in conjugation with the arising carbocation. If the steric hindrance prevents the conjugation, the rate of the reaction may become over two orders of magnitude smaller: The steric constants $-E_s'$ calculated from the kinetic effects are for phenyl and methyl 2.31 and 0.0 respectively [7].

In butanol where dominates the electrophilic solvation resulting from hydrogen bonds with nucleofuge, the phenyl group is conjugated with the arising carbocation. This is manifested by the heterolysis rate 3 orders of magnitude lower for phenyl derivatives compared to methyl derivatives, At the lack of this conjugation the heterolysis rates of methyl and phenyl derivatives should not be very different since the σ_p^E values of Me and Ph are similar: -0.30 and -0.18 respectively [7]. The ΔS^\ddagger values show that in solvolysis of chlorides **IV** and **V** prevails the effect of the damaging solvent structure, and in solvolysis of bromides **VI** and **VII**, electrostriction effect. Chlorine forms a stronger hydrogen bond with the alcohol molecules and therefore stronger damages the solvent structure. The coordination of a single monodentate ligand is known to reduce the ΔS^\ddagger by $\sim 45 \text{ J mol}^{-1}\text{K}^{-1}$ [16]. Consequently, in solvolysis of bromide **VI** during the formation of the transition state at least one solvent molecule is involved, and in solvolysis of bromide **VII**, two molecules.

The pattern in sulfolane is quite different: The heterolysis rate does not change in going from methyl to phenyl derivatives, and the ΔH^\ddagger value is higher for the phenyl derivatives. In this dipolar aprotic solvent (μ 4.8 D) electrostatic dipole-dipole solvation occurs that considerably stronger affects the formation of the transition state in the heterolysis of the methyl than the phenyl derivatives. This results apparently from the steric hindrances originating from the phenyl group. The ΔS^\ddagger values show that in formation of the transition state in the heterolysis of chloride **IV** one solvent molecule is involved, in the case of bromide **VII** three molecules, whereas in the heterolysis of the phenyl derivatives practically no additional solvation occurs during the

transition state formation. The latter is likely due to the strong dipolar solvation of the covalent substrates (initial states) of the phenyl derivatives which prevents the conjugation of the phenyl group with the arising carbocation. As a result the heterolysis rate of the phenyl derivatives in sulfolane is ~ 2 orders of magnitude smaller than in butanol, whereas the methyl derivatives characterized by no steric hindrances are more active in sulfolane.

EXPERIMENTAL

2-Halo-2-alkyladamantanes **IV–VII** were prepared reacting the corresponding alcohols with PCl_3 (PBr_3) [10, 17, 18]. To a dry alcohol was added dropwise a three-fold excess of PCl_3 (PBr_3), the product was extracted with petroleum ether of pentane, the extract was washed with water solution of potassium carbonate and water till neutral washings, dried with Na_2SO_4 , evaporated to dryness, and the residue was thrice recrystallized from MeCN. Yields 60–70%. Compound **IV**, mp 174°C (publ.: mp 176°C [17]), compound **V**, mp 131°C (publ.: mp 133°C [17]), compound **VI**, mp 132°C (publ.: mp $132\text{--}135^\circ\text{C}$ [19]), compound **VII**, mp 125°C (publ.: mp 126°C [20]).

1,3,5-Triphenylverdazyl was synthesized and purified as described in [21]. UV spectrum, λ_{max} (ϵ): 710 (4000) in BuOH; 720 (3910) in sulfolane. The solvents were dried over CaO and subjected to rectification.

Kinetic experiments were performed in a temperature-controlled cell of a spectrophotometer SF-26. Substrate concentration in the kinetic runs was $0.01\text{--}0.6 \text{ mol l}^{-1}$, that of verdazyl indicator, $(1\text{--}3)\times 10^{-4} \text{ mol l}^{-1}$. The conversion of the substrate in a run was $0.1\text{--}0.01\%$. The average of three runs was evaluated, the error was $\sim 5\%$. The rate constants at various temperatures are available from the authors.

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