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Kinetics and Mechanism of Monomolecular Heterolysis of Commercial Organohalogen Compounds: XL.[1] Nature of Salt Effects in Dehydrobromination of 3-Bromocyclohexene in γ-Butyrolactone. Role of Solvation Effects of Dipolar Aprotic Solvents

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Abstract—The influence of neutral salts on the rate of heterolysis of 3-bromocyclohexene at 31°C in γ-butyrolactone was studied by the verdazyl method; $v = k[C_6H_9Br]$, E1 mechanism. Additions of lithium picrate do not affect the reaction rate; those of $LiClO_4$ and Et_4NClO_4 increase it; and those of LiCl, Et_4NCl, and KNCS decelerate the reaction. The nature of salt and solvation effects in the heterolysis of 3-bromocyclohexene in γ-butyrolactone, MeCN, and $PhNO_2$ is discussed.

The rate of monomolecular heterolysis (S_N1, E1, solvolysis) is controlled by the ionization of a covalent bond, occurring via successive formation of three ion pairs: contact **I**, spacially separated **II**, and solvation-separated **III** [2]:

$$\underset{}{RX} \rightleftharpoons \underset{\mathbf{I}}{R{+}X^-} \rightleftharpoons \underset{\mathbf{II}}{R^+\cdots X^-} \rightleftharpoons \underset{\mathbf{III}}{R^+|Solv|X^-} \longrightarrow \text{Reaction products.} \quad (1)$$

In the limiting step, pair **I** interacts with a solvent cavity (cavities account for ~10% of the volume of a liquid [3]). Ion pair **II** is thus formed, which rapidly transforms into ion pair **III** which, in turn, rapidly yields the reaction products.

Neutral salts (ammonium or alkali metal salts) affect the heterolysis rate strongly and specifically [4–7]. The nature and intensity of the salt effect depend on the substrate structure, salt, and solvent. The observed diversity of the salt effects is due to the fact that an ion pair of a salt or its ions can interact with a covalent substrate or various ion-pair intermediates [6, 7].

When a salt acts on a covalent substrate, the reaction rate linearly grows with the salt concentration (normal salt effect). The value of this effect (*b*, $l\ mol^{-1}$) is calculated by Winstein equation (2) [8], where k_s and *k* are the rate constants of the reaction in the presence of a salt and without it.

$$k_s = k(1 + b[\text{salt}]). \quad (2)$$

The linear character of the normal salt effect is due to the low constant of association of a salt with a covalent substrate; the parameter *b* reflects this association constant.

When a salt acts on pair **I**, the reaction rate first sharply increases, but further additions of the salt do not longer affect the reaction rate, and $dk/d[\text{salt}] = 0$ (special salt effect). The association constant of the salt with pair **I** is high; therefore, even at low concentrations of the additive (10^{-2}–10^{-4} M), the ion pair is virtually fully bound by the salt to form a quadrupole or a ternary ionic associate, and further additions of the salt exert no effect on the reaction rate.

Usually a superposition of the normal and special salt effects is observed: The reaction rate first sharply increases at low salt concentrations, and then the increase becomes more gradual. Extrapolation of the linear portion of the curve to [salt] = 0 gives the maximal value of the special salt effect (k_{ext}). The parameters b_1 and b_2 characterizing the association of a salt with pair **I** and covalent substrate are calculated from the first and second portions of the curve by Eq. (2). Usually $b_1 : b_2 \approx 10–10^2$.

When a salt acts on intermediates formed after the limiting step (pairs **II** , **III**), the reaction rate first drastically decreases, but further addition of the salts do not affect the rate, and $dk/d[\text{salt}] = 0$ (negative special salt effect). Extrapolation of the second portion of the curve to [salt] = 0 gives the maximal value of this salt

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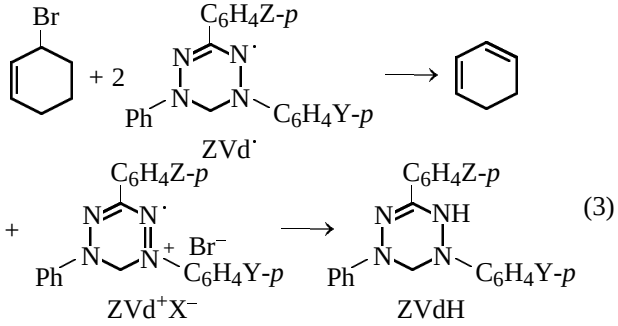
effect (k_{min}), and the ratio $k_{min} : k$ indicates what part of the associate of the salt with pair **III** gives the reaction product. The parameter *b* reflecting the association constant of the salt with pair **III** is calculated from the first portion of the curve by Eq. (2). At a normal salt effect, a salt catalyzes transformation of a covalent substrate into pair **I**, and under the conditions of a special salt effect a salt facilitates the ion separation in pair **I**; the negative special salt effect is associated with the catalysis of the return of the external pair (**III**–**II**–**I**–RX) [6, 7].

At a superposition of the positive and negative salt effects, the *k*–[salt] plot may pass through a maximum. This was the case in heterolysis of PhCHClMe in γ-butyrolactone in the presence of Bu_4NBr [9], of Ph_2CCl_2 in MeCN in the presence of LiBr [10], and of 7α-bromocholesterol benzoate in *o*-xylene in the presence of *N*-cetylpyridinium bromide [11].

The site of the effect of the salt anion on the heterolysis reaction coordinate is determined by the principle of hard and soft acids and bases [12]. The harder the anion, the more readily is interacts with a harder electrophile in scheme (1). In particular, in heterolysis of 1-AdOTs and 1-AdOPic (OPic is picrate) in aprotic solvents in the presence of ammonium perchlorate, bromide, and chloride, the ClO_4^- anion acts on the covalent substrate (normal salt effect); Br^-, on pair **I** (special salt effect); and Cl^-, on pair **III** (negative special salt effect) [13].

In the previous studies of this series [14, 15], we examined by the verdazyl method [16] the effect of various salts on the rate of heterolysis of 3-bromocyclohexene **IV** in $PhNO_2$. As internal triphenylverdazyl indicators ZVd$^\cdot$ we used 1,3,5-triphenylverdazyl (HVd$^\cdot$), 1,5-diphenyl-3-(4-chlorophenyl)verdazyl (ClVd$^\cdot$), 1,5-diphenyl-3-(4-nitrophenyl)verdazyl (NO_2Vd$^\cdot$), and 1-phenyl-3,5-di(4-methoxyphenyl)verdazyl (MeOVd$^\cdot$), which rapidly and quantitatively react with pair **III** of the substrate to form cyclohexa-1,3-diene, verdazylium salt ZVd$^+$Br$^-$, and leucoverdazyl ZVdH. The reaction follows Eq. (3).



(3)

ZVd$^\cdot$, Z = Y = H (HVd$^\cdot$); Z = Cl, Y = H (ClVd$^\cdot$); Z = NO_2, Y = H (NO2Vd$^\cdot$); Z = Y = OMe (MeOVd$^\cdot$).

The reaction rate was monitored spectrophotometrically by the decrease in the ZVd$^\cdot$ concentration; it is satisfactorily described by first-order kinetic equation (4) and is independent of the concentration and structure of the verdazyl indicator.

$$-d[\text{ZVd}^\cdot]/2dt = k[(\mathbf{IV})]. \quad (4)$$

We showed that additions of LiOPic do not affect the reaction rate, perchlorates exert a normal salt effect, in the presence of bromides there is a superposition of the normal and special salt effects, and in the presence of chlorides the *k*–[salt] plot passes through a maximum, suggesting a superposition of the positive and negative salt effects. In all the cases, the acting salt agent is the anion.

With perchlorates, the value of the normal salt effect (*b* 16) is independent of particular verdazyl indicator, and with bromides the values of the salt effects ($k_{ext} : k$ = 1.4, b_1 400, b_2 50) are independent of the substituent in the C-phenyl ring of verdazyl. With MeOVd$^\cdot$, only the normal salt effect is observed (*b* 60). In the presence of chlorides, the extent to which the reaction rate increases in the first portion of the *k*–[salt] curve and the rate constant in the region of the maximum grow with an increase in the electron-donor power of the verdazyl indicator in the series NO_2Vd$^\cdot$–ClVd$^\cdot$–HVd$^\cdot$, and the extent to which the reaction rate decreases after passing through the maximum grows in the opposite order. Hence, the value of the negative salt effect grows with an increase in the electron-acceptor power of ZVd$^\cdot$ With MeOVd$^\cdot$ in the presence of chlorides, only the normal salt effect is observed (*b* 60).

The specific behavior of chlorides and bromides with the MeOVd$^\cdot$ indicator is accounted for by formation in heterolysis of bromide **IV** of two pairs **I** differing in the activity [16–18].

Data obtained in $PhNO_2$ [14, 15] show that a salt can interact simultaneously with both the covalent substrate and various cationoid intermediates; the intensity of this interaction is determined by the principle of hard and soft acids and bases [12]. The polyfunctonal effect of a salt is revealed in some cases when studying the normal salt effect. In particular, in heterolysis of Ph_2CHBr in acetone [19] and MeCN [20] and also of Ph_2CHCl in γ-butyrolactone [1] in the presence of $LiClO_4$, the normal salt effect grows with an increase in the electron-acceptor power of the verdazyl indicator in the series MeOVd$^\cdot$ < HVd$^\cdot$ < NO_2Vd$^\cdot$. This means that actually we deal with a superposition of the positive and negative salt effects, with the latter decreasing with an increase of the elec-

tronegativity of the verdazyl. In these cases, the acting agent was the salt anion, as in the heterolysis of **IV** in $PhNO_2$. However, in the heterolysis of Ph_2CHBr [21] and 1-AdI [22] in γ-butyrolactone in the presence of $LiClO_4$, the acting agent of the salt is its ion pair or the Li^+ cation, and the negative salt effect is enhanced with an increase in the electron-donor power of ZVd·.

The effect of salts on the rate of the heterolysis of **IV** in MeCN [23] strongly differs from that observed in $PhNO_2$. Additions of $LiClO_4$, LiBr, Et_4NBr, and Et_4NCl do not affect the rate, and in the presence of iodides (Et_4NI, *N*-butylquinolinium iodide, KI) only the normal salt effect is observed, which is independent of the salt cation and substituent in the phenyl ring of the verdazyl. Here the acting agent is iodide ion, which nucleophilically assists the heterolysis.

Proceeding with studies of salt effects in the heterolysis of bromide **IV**, we examined by the verdazyl method [16] the effect of LiOPic, LiClO4, Et_4NClO_4, LiBr, Et_4NBr, LiCl, Et_4NCl, and KCNS additions on the rate of the heterolysis of this substrate in γ-butyrolactone at 31°C. As internal indicators we used HVd·, MeOVd·, and NO_2Vd·. The reaction follows stoichiometric equation (3). The reaction rate in the presence of salts and without them is satisfactorily described by kinetic equation (4).

Without salt additions, $k_{31} = (7.75 \pm 0.20) \times 10^{-6}$ s^{-1}. Additions of LiOPic exert no effect on the reaction rate (Fig. 1, curve *2*); at LiOPic concentrations of ~$(4–30) \times 10^{-3}$ M, $k = (7.95 \pm 0.28) \times 10^{-6}$ s^{-1}. In the presence of perchlorates, a superposition of the normal and special salt effects is observed (Fig. 1, curve *1*), $k_{ext} = 8.36 \times 10^{-6}$ s^{-1}, b_1 150, b_2 3.4. The maximal value of the special salt effect exceeds the reaction rate without salt additions by a factor of ~1.1 (usually this ratio is within 1.1–4 [6]). The reaction rate is independent of the salt cation; the acting agent is the ClO_4^- anion.

Chlorides, bromides, and KCNS decelerate the reaction (Fig. 1, curves *2*–*5*). The values of these salt effects are independent of the cation; hence, the acting agent of these salts is the anion.

The negative salt effect is accounted for by the action of a salt on pair **III** or **II** [6, 7]. In the first case, the reaction rate should depend on the concentration and structure of the verdazyl indicator, since ZVd· and the salt act on the same intermediate; in the second case, such dependences should be lacking [24].

Figure 2 shows how the concentration and structure of the indicator affect the reaction rate in the presence of 0.025 M Et_4NBr or 0.020 M Et_4NCl. In the presence of the bromide, the reaction rate decreases to

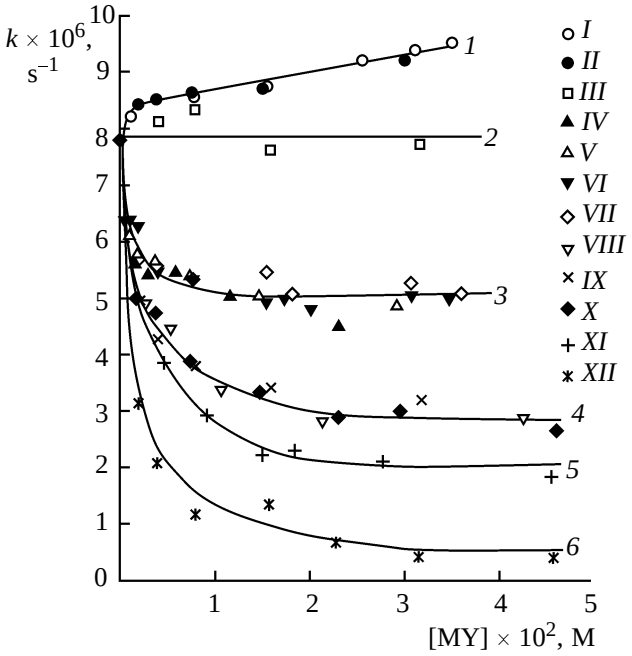


Fig. 1. Salt effect on the rate of heterolysis of 3-bromocyclohexene in γ-butyrolactone, 31°C: (*1*) influence of the concentration of (*I*) $LiClO_4$ and (*II*) Et_4NClO_4, HVd· indicator; (*2*, *III*) influence of the LiOPic concentration, HVd· indicator; (*3*) influence of the concentration of (*IV*) LiBr, HVd· indicator, and of Et_4NBr, indicator (*V*) HVd·, (*VI*) MeOVd·, and (*VII*) NO_2Vd·; (*4*) influence of the concentrations of (*VIII*) LiCl and (*IX*) KCNS, HVd· indicator, and of (*X*) Et_4NCl, MeOVd· indicator; (*5*, *XI*) influence of the Et_4NCl concentration, HVd· indicator; and (*6*, *XII*) influence of the Et_4NCl concentration, NO_2Vd· indicator.

~5.2×10^{-6} s^{-1} and at [HVd·] > 5×10^{-5} M is independent of the indicator concentration (Fig. 2, curve *1*). At lower HVd· concentrations, the reaction rate depends on [HVd·], because such concentrations are insufficient to adequately monitor the reaction rate (at [HVd·] = 0, the measured reaction rate is zero). In the presence of Et_4NCl, the reaction rate depends on both the concentration and structure of the verdazyl indicator; in the presence of NO_2Vd· (Fig. 2, curve *3*), the rate is lower than in the presence of MeOVd· (Fig. 2, curve *2*).

These data show that a decrease in the reaction rate in the presence of chlorides and bromides is due to the action of chlorides on pair **III** and of bromides on pair **II** or another intermediate preceding formation of pair **II**. These conclusions are consistent with data in Fig. 1 showing how the rate of heterolysis of **IV** depends on the salt concentration with various verdazyl indicators.

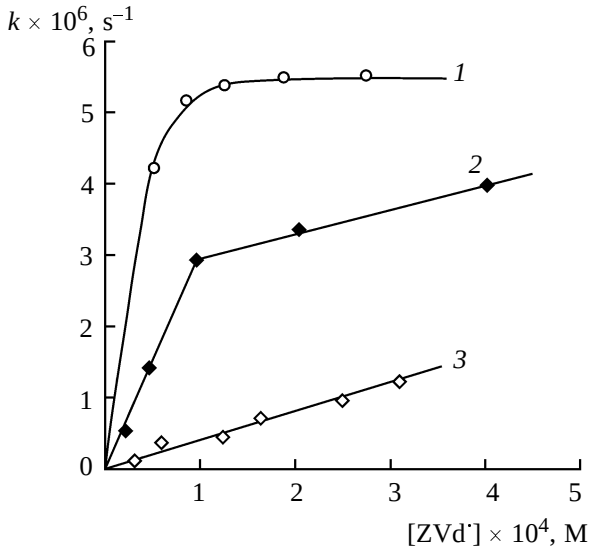
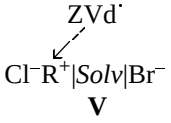


Fig. 2. Influence of the ZVd$^{\cdot}$ concentration on the rate of heterolysis of 3-bromocyclohexene in γ-butyrolactone, 31°C: (*1*) HVd$^{\cdot}$, 0.025 M Et_4NBr; (*2*) MeOVd$^{\cdot}$, 0.020 M Et_4NCl; and (*3*) $NO_2Vd^{\cdot}$ concentration, 0.020 M Et_4NCl.

The rate of heterolysis of bromide **IV** at $[Et_4NBr] \geq 0.003$ M (Fig. 1, curve *2*) is independent on the salt concentration and structure of the verdazyl indicator (b 25.0 l mol^{-1}, k_{min} 5.2×10^{-6} s^{-1}, $k_{min} : k = 0.67$). Hence, the bromide anion acts on an intermediate preceding the formation of pair **III** and at $[Et_4NBr] \geq 0.003$ M completely binds this intermediate. Therefore, the minimal rate constant in Fig. 1, curve *2* and the maximal rate constant in Fig. 2, curve *1* are equal: ~5.2×10^{-6} s^{-1}. Under these conditions, 33% of the salt–intermediate associate transforms back into the covalent compound. Direct action of Br^- on pair **II** is improbable, since the lifetime of this intermediate is restricted by the time of translation–rotation relaxation of the solvent dipole (~10^{-11} s [25, 26]). This means that pair **II** transforms into pair **III** at a rate of ~10^{11} s^{-1}, whereas the rate of diffusion contact of the salt anion with pair **II** is considerably lower {5×10^9 l mol^{-1} s^{-1}) [27]}. The negative salt effect in this case can be accounted for by the action of salt M^+Y^- on pair **I** with the formation of a ternary anionic complex $Y^-R^+X^-$, which, upon interaction with a solvent cavity, transforms into a spacially separated ternary associate $Y^-R^+\cdots X^-$, which, in turn, can transform back into the covalent substrate with the formation of the nucleofuge exchange product RY (initial substrate in our case).

A more probable explanation of the negative salt effect of the bromide is the action of the salt on an ion pair separated by one solvent molecule, which is formed from pair **II** and subsequently transforms into ion pair **III** separated by two solvent molecules [5]. A quantum-chemical analysis of the separation of ions in a liquid registers the formation of both these ion pairs [28].

Chlorides decrease the reaction rate more strongly than do bromides (Fig. 1, curves *3–5*); Cl^- acts on a later intermediate, pair **III**. This is consistent with the principle of hard and soft acids and bases [13–15]. In this case, the reaction rate depends on the concentration and structure of ZVd$^{\cdot}$ and at $[Et_4NCl] \geq 0.015$ M is independent of the salt concentration. At these concentrations, Cl^- completely binds ion pair **III** to form a ternary anionic associate $Cl^-R^+|Solv|Br^-$. Therefore, the rate constants plotted in Fig. 1, curves *3*, *5* at $dk/d[salt] = 0$ and [ZVd$^{\cdot}$] ≥ 1.5×10^{-4} M and the rate constants plotted in Fig. 2, curves *2*, *3* at the same concentrations of verdazyl indicators essentially coincide, which indicates that, at $[Et_4NCl] \geq 0.015$ M, the verdazyl indicator is completely bound by the ternary associate $Cl^-R^+|Solv|Br^-$ to form charge-transfer complex **V**:



V

The parameters of the negative special salt effect in the presence of bromides are as follows: with MeOVd$^{\cdot}$, b –190 l mol^{-1}, k_{min} 3.2×10^{-6} s^{-1}, $k_{min} : k = 0.41$; with HVd$^{\cdot}$, b –120 l mol^{-1}, k_{min} 2.0×10^{-6} s^{-1}, $k_{min} : k = 0.26$; with $NO_2Vd^{\cdot}$, b –80 l mol^{-1}, k_{min} 0.6×10^{-6} s^{-1}, $k_{min} : k = 0.08$. The above values of b show that the constants of formation of complexes **V** increase with in an increase in the electron-donor power of ZVd$^{\cdot}$, and the degree of transformation of these complexes into the covalent substrate increases in the opposite direction: 59% for MeOVd$^{\cdot}$, 74% for HVd$^{\cdot}$, and 92% for $NO_2Vd^{\cdot}$.

A decrease in the reaction rate in the presence of chlorides is due to the fact that complex **V** formed when Cl^- and ZVd$^{\cdot}$ act on pair **III** can transform along two pathways: into the reaction products and back into the covalent substrate [6, 7].

Formation of the reaction products is a multistep process in which the limiting step is either formation of complex **V** or its decomposition into ZVd^+Br^- and alkyl radical which rapidly reacts with a second verdazyl molecule to form the alkylation product Vd–R, decomposing by an E1 reaction into the the olefin and leucoverdazyl. If formation of **V** is the limiting step, the reaction rate should grow with an increase in the electron-donor power of ZVd$^{\cdot}$, and if the decomposi-

tion of **V** is the limiting step, the trend will be opposite.

The second reaction pathway (return) is due to strong delocalization of the carbocation charge in **V** over three ligands: Br^-, Cl^-, and ZVd· As a result, the bond with the fourth ligand, a solvent molecule occurring in the interionic space, becomes weaker, and this molecule readily passes into the cavity arising in the vicinity of the complex. Pair **II** thus formed transforms into pair **I**, which then rapidly "collapses" to form the covalent substrate [6, 7]. The rate of the reaction along this pathway should grow with an increase in the electron-donor power of ZVd·

Thus, the rate of formation of reaction products under the conditions of the negative special salt effect can grow with an increase in both electron-donor and electron-acceptor power of ZVd·, and the return rate, only with an increase in the electron-donor power of the indicator. As a result of a competition between these two pathways, the dependences of the negative salt effect on the substituent in the verdazyl indicator may be diverse, which is actually the case [6, 7, 22].

In our case, the negative special salt effect becomes stronger with an increase in the electron-acceptor power of ZVd· This fact indicates that both reaction pathways involve formation of complex **V** as the limiting step and that an increase in the electron-donor power of verdazyl exerts a stronger effect on the product formation than on the return.

In the heterolysis of Ph_2CHBr [22] and 1-AdI [21] in γ-butyrolactone in the presence of $LiClO_4$, the negative special salt effect becomes stronger with an increase in the electron-donor power of ZVd· In these cases, the acting agent of the salt is the ion pair which, apparently, forms a cyclic quadrupole with pair **III**:

$$R^+|Solv|Br^-$$

$$ClO_4^-|Solv|Li^+$$

Complex **V** formed when ZVd· acts on this quadrupole has also two reaction pathways; the product formation depends on the electron-donor power of ZVd· to a lesser extent than does the return.

As expected, the salt effects in the heterolysis of **IV** strongly depend on the solvent. In going from MeOH to toluene, the rate of the heterolysis of **IV** decreases by 5 orders of magnitude [29]. In dipolar aprotic solvents, various solvates can form, which react at different rates and differently interact with salts. We studied the salt effects in three dipolar aprotic solvents having similar dielectric permittivity (ε) but strongly differing in the electrophilicity (*E*) and nucleophilicity (*B*) parameters [30]: MeCN, ε 37.5, *E* 22, *B* 1.9; γ-butyrolactone, ε 39.0, *E* 12, *B* 2.5; $PhNO_2$, ε 34.5, *E* 1.0, *B* 0.8.

Effect of aprotic solvent on the kinetic parameters of the heterolysis of 3-bromocyclohexene and Ph_2CHBr

Solvent	$-\log k_{25}$, k in s^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}	$\Delta G^{\neq}$, kJ mol^{-1}
γ-Butyrolactone	5.38 (5.63)[a]	92 (87)	40 (64)	104 (105)
MeCN	5.50 (5.60)	72 (69)	110 (122)	104 (105)
$PhNO_2$	7.00 (7.39)	86 (68)	90 (157)	113 (115)

[a] In parentheses are data for Ph_2CHBr.

In the heterolysis of **IV** in MeCN, which is a strong (compared to nitrobenzene and γ-butyrolactone) CH acid (pK_a 24 [31]), bromides and chlorides do not affect the reaction rate, and iodides exert a normal salt effect due to the nucleophilic assistance to the heterolysis, rendered by I^- [23]. Presumably, the bromide and chloride anions are deactivated owing to formation of an H complex $Y^-\cdots\rightarrow{}^{\delta+}H{-}CH_2CN^{\delta-}$, and only the iodide ion, thanks to its large size and high polarizability, preserves its activity. However, in the heterolysis in MeCN of such secondary substrates as Ph_2CHBr [32] and Ph_2CHCl [33], when the nucleophilic attack from the rear side is possible, additions of chlorides, bromides, iodides, and nitrates strongly decelerate the reaction, with the salt anion being the acting agent.

To account for the differences observed in the salt effects in the heterolysis of bromide **IV** and benzhydryl halides, it is necessary to consider the solvation effects for these substrates. The rate of the heterolysis of both 3-bromocyclohexene and diphenylbromomethane depends on the polarity and electrophilicity of the solvent, or on its ionizing power [29, 34]; the solvent effect is considerably stronger with Ph_2CHBr. For 9 protic and 14 aprotic solvents, the following correlation was obtained:

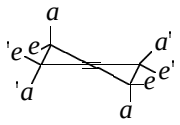
$$\log k_{\mathbf{IV}} = 1.71 + 0.719\log k_{Ph_2CHBr},$$
$$R\ 0.989,\ S\ 0.24,\ n\ 23.$$

The kinetic parameters of the heterolysis of bromide **IV** and Ph_2CHBr in MeCN, $PhNO_2$, and γ-butyrolactone [14, 15, 22, 35, 36] are listed in the table. In all the solvents, the rate of the heterolysis of Ph_2CHBr is slightly lower than that of **IV**, although the activation enthalpy in heterolysis of Ph_2CHBr is always

lower than that of **IV**. The decrease in the heterolysis rate in going from **IV** to Ph_2CHBr is due to a decrease in the activation entropy.

Low values of $\Delta S^{\neq}$ in the heterolysis of Ph_2CHBr are indicative of strong steric hindrance arising in the solvation of the transition state.

A specific feature of bromide **IV** is that it is more accessible than Ph_2CHBr to a nucleophilic attack from the rear side. The most stable conformer of cyclohexene is half-chair **VI** in which the allyl bonds (pseudo-axial *a*' and pseudo-equatorial *e*') form a torsion angle of 59°, which makes the carbon atom in these positions readily accessible to a nucleophilic attack from the rear side [37]. As a result, bromide **IV** is readily solvated from the rear side with an MeCN molecule, which prevents the nucleophilic assistance of the heterolysis by such ions as Br^- and Cl^-, and only the large and readily polarizable iodide anion can overcome the solvation effect of MeCN. It is known that, in solvolysis of optically active PhCHClMe, additions of alkyl cyanides favor the configuration retention, which is attributed to the blocking effect of RCN molecules on the nucleophilic attack from the rear side [38].



VI

Among the solvents under consideration, γ-butyrolactone is the most basic. In this solvent, salts exist in form **III**, whereas in MeCN they form pair **I** [39]. Therefore, in γ-butyrolactone salts readily interact with pair **III** of the substrate to form cyclic quadrupoles. Also, in heterolysis of various substrates in γ-butyrolactone, $\Delta S^{\neq}$ (about –50 J mol^{-1} K^{-1}) is usually appreciably higher than in other dipolar aprotic solvents (about –120 J mol^{-1} K^{-1}) [10, 11, 21, 22, 40–44]. This fact suggests relatively weak solvation of the transition state, which makes the cationoid intermediate readily accessible for association with an ion pair or anion of a salt. Therefore, in γ-butyrolactone, the majority of salts (even perchlorates [20, 21], which, as a rule, accelerate the reaction [6, 22]) exert a negative special salt effect. This was observed in the heterolysis of Ph_2CHBr [19, 40], t-BuCl and 2-chloro-2-methyladamantane [41], 7α-bromocholesterol benzoate [11], Ph_2CCl_2 [10], 1-AdOTs and 1-AdOPic [42], cumyl chloride [43], and 2-bromo-2-methyladamantane [44]. As in the heterolysis of bromide **IV**, the negative special salt effect usually becomes stronger with an increase in the electron-acceptor power of ZVd$^{\cdot}$; only in the presence of $LiClO_4$ the trend is opposite.

In nitrobenzene, which is a weak nucleophile and a weak electrophile simultaneously, the *k*–[salt] dependence in the heterolysis of **IV** in the presence of chlorides passes through a maximum [14, 15] reflecting a superposition of positive and negative salt effects. However, in the heterolysis of 1-AdOPic [42] and 7α-bromocholesterol [11], when solvation is weaker than in the heterolysis of **IV** (as judged from $\Delta S^{\neq}$, about ~50 J mol^{-1} K^{-1}), only a negative special salt effect is observed in the presence of chlorides.

Thus, a combined consideration of the salt and solvation effects allows more comprehensive understanding of the mechanisms of both effects.

EXPERIMENTAL

3-Bromocyclohexene was prepared and purified as in [29], and triphenylverdazyls, as in [45]. γ-Butyrolactone was kept for 40 h over anhydrous $CaCl_2$, filtered, kept for 1 h over P_2O_5, decanted, distilled in a vacuum, kept over K_2CO_3 for 30 h, filtered, and double-distilled in a vacuum; bp 70°C (8 mm Hg). Salts were recrystallized from ethanol or acetone and dried in a vacuum (2–3 mm Hg) at 110°C.

The kinetic experiments were performed in a temperature-controlled cell of an SF-26 spectrophotometer. The reaction rate was monitored by a decrease in the ZVd$^{\cdot}$ concentration (for MeOVd$^{\cdot}$, λ_{max} 750 nm, ε 4470 l mol^{-1} cm^{-1}; for HVd$^{\cdot}$, λ_{max} 720 nm, ε 4360 l mol^{-1} cm^{-1}; and for NO_2Vd$^{\cdot}$, λ_{max} 740 nm, ε 4200 l mol^{-1} cm^{-1}). The conversion of **IV** in the kinetic runs did not exceed ~0.6%; the determination errors were ±(3–4)%.

Below are the temperature (°C) and $k \times 10^6$ (s^{-1}): 26.5, 4.94; 31.0, 7.75; 34.6, 14.1; 40.0, 24.9; 44.0, 40.5.

Below are the salt, ZVd$^{\cdot}$, salt concentration (M), [ZVd$^{\cdot}$] × 10^4 (M), and $k \times 10^6$ (s^{-1}): LiClO4, HVd$^{\cdot}$, 1.07×10^{-1}, 1.50, 8.22; 7.75×10^{-3}, 2.00, 8.56; 1.55×10^{-2}, 2.50, 8.75; 2.55×10^{-2}, 1.60, 9.21; 3.11×10^{-2}, 2.5, 9.40; 3.50×10^{-2}, 1.50, 9.53. Et_4NClO_4, HVd$^{\cdot}$, 1.88×10^{-3}, 1.82, 8.43; 3.75×10^{-3}, 1.82, 8.51; 7.50×10^{-3}, 1.82, 8.63; 1.50×10^{-2}, 1.82, 8.72; 3.00×10^{-2}, 1.82, 9.20. LiOPic, HVd$^{\cdot}$, 3.95×10^{-3}, 1.71, 8.13; 7.90×10^{-3}, 1.97, 8.34; 1.58×10^{-2}, 1.50, 7.63; 3.16×10^{-2}, 1.50, 7.72. LiBr, HVd$^{\cdot}$, 1.43×10^{-3}, 1.34, 5.65; 2.87×10^{-3}, 1.63, 5.44; 5.75×10^{-3}, 1.63, 5.49; 1.15×10^{-2}, 1.63, 5.06; 2.30×10^{-2}, 1.63, 4.53. Et_4NBr, HVd$^{\cdot}$, 9.10×10^{-4}, 1.31, 6.14; 1.82×10^{-3}, 1.43, 5.79; 3.65×10^{-3}, 1.55, 5.69; 7.30×10^{-3}, 1.85, 5.41; 1.46×10^{-2}, 1.35, 5.05; 2.92×10^{-2}, 1.35, 4.89. Et_4NBr, MeOVd$^{\cdot}$, 4.80×10^{-4}, 1.47, 6.38; 9.60×10^{-4}, 1.47, 6.38; 1.92×10^{-3},

1.47, 6.26; 3.85×10^{-3}, 1.47, 5.46; 7.70×10^{-3}, 1.37, 5.33; 1.54×10^{-2}, 1.37, 4.91; 1.73×10^{-2}, 1.50, 4.98; 2.01×10^{-2}, 3.10, 4.79; 3.08×10^{-2}, 1.37, 5.04; 3.47×10^{-2}, 1.60, 4.97. Et_4NBr, $NO_2Vd^{\cdot}$, 1.92×10^{-3}, 1.89, 5.69; 3.85×10^{-3}, 2.10, 5.56; 7.70×10^{-3}, 1.70, 5.33; 1.54×10^{-2}, 1.70, 5.45; 1.80×10^{-2}, 2.20, 5.06; 3.07×10^{-2}, 1.70, 5.26; 3.60×10^{-2}, 1.90, 5.10. Et_4NBr, $HVd^{\cdot}$, 2.54×10^{-2}, 0.52, 4.21; 2.54×10^{-2}, 0.86, 5.16; 2.54×10^{-2}, 1.26, 5.38; 2.54×10^{-2}, 1.88, 5.50; 2.54×10^{-2}, 2.75, 5.52. KCNS, $HVd^{\cdot}$, 2.00×10^{-3}, 1.40, 4.95; 3.97×10^{-3}, 1.88, 4.28; 7.94×10^{-3}, 1.88, 3.79; 1.59×10^{-2}, 1.88, 3.41; 3.18×10^{-2}, 1.88, 3.19. LiCl, $HVd^{\cdot}$, 2.66×10^{-3}, 1.50, 4.88; 5.32×10^{-3}, 1.50, 4.44; 1.06×10^{-2}, 1.50, 3.35; 2.13×10^{-2}, 1.50, 2.80; 4.26×10^{-2}, 1.46, 2.84. Et_4NCl, $HVd^{\cdot}$, 4.60×10^{-3}, 1.60, 3.85; 9.20×10^{-3}, 1.60, 2.93; 1.50×10^{-2}, 1.60, 2.22; 1.84×10^{-2}, 1.60, 2.29; 2.77×10^{-2}, 2.15, 2.10; 4.55×10^{-2}, 2.15, 1.83. Et_4NCl, $MeOVd^{\cdot}$, 1.83×10^{-3}, 1.68, 4.99; 3.66×10^{-3}, 1.47, 4.74; 7.35×10^{-3}, 1.47, 3.86; 1.47×10^{-2}, 1.47, 3.32; 2.30×10^{-2}, 1.90, 2.89; 2.95×10^{-2}, 1.47, 2.99; 4.60×10^{-2}, 1.40, 2.64. Et_4NCl, $NO_2Vd^{\cdot}$, 1.97×10^{-3}, 2.10, 3.16; 3.94×10^{-3}, 1.90, 2.10; 7.87×10^{-3}, 1.36, 1.19; 1.57×10^{-2}, 1.36, 1.38; 2.28×10^{-2}, 1.64, 0.713; 3.15×10^{-2}, 1.36, 0.448; 4.57×10^{-2}, 1.64, 0.422. Et_4NCl, $MeOVd^{\cdot}$, 2.05×10^{-2}, 0.22, 0.540; 2.05×10^{-2}, 0.47, 1.43; 2.05×10^{-2}, 0.96, 2.93; 2.05×10^{-2}, 2.05, 3.35; 2.05×10^{-2}, 4.02, 3.99. Et_4NCl, $NO_2Vd^{\cdot}$, 2.02×10^{-2}, 0.31, 0.123; 2.02×10^{-2}, 0.60, 0.375; 2.02×10^{-2}, 1.24, 0.442; 2.02×10^{-2}, 2.50, 0.964; 2.02×10^{-2}, 3.10, 1.23.

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