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Interpretation Paradoxes in Unimolecular Heterolysis Kinetics

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Abstract—The rate constant of the first-order rate equation $w = k[\mathrm{RX}]$ that is derived from the variation of the reaction product concentration or determined by the verdazyl method characterizes the lifetime of the transition state or that of the solvent-separated ion pair rather than the heterolysis rate. The diffusion rate constant is equal to the dissociation rate constant of the contact ion pair and to the reverse of the lifetime of the solvent-separated ion pair: $k_D \approx k = 1/\tau \approx 10^{10}$ s^{-1}.

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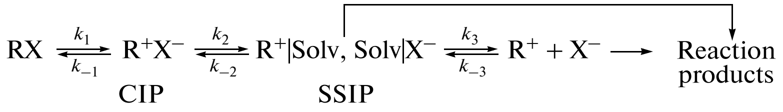
The most typical first-order reactions are those involving the dissociation of a covalent bond (heterolysis, homolysis, carbenolysis). They include substitution, addition, isomerization, various rearrangements. The first step of these reactions yields reactive intermediates, which determine their specific kinetic features [1–3]. Among the first-order reactions, unimolecular heterolysis reactions (S_N1, E1, F1, solvolysis) have been investigated most comprehensively. Elucidation of the mechanisms of these reactions is of fundamental importance for understanding the reactivity of organic compounds. These mechanisms have permanently been investigated for more than 80 years [4–6]. The rate-limiting step of heterolysis yields a cationoid intermediate (Int), which determines the specific features of the overall reaction. The unimolecular heterolysis rate $w = k[\mathrm{RX}]$ increases greatly (by approximately 10 orders of magnitude) as the polarity of the solvent is increased [6]. These reactions are very slow. For example, it would take about 1 year for the heterolysis of *t*-BuCl in *n*-BuOH at 25°C to proceed to an extent of 50%. The same reaction in $PhNO_2$ would take ~200 years ($\tau_{1/2} = 0.693/k$) [7].

In the last 60 years, the mechanism of unimolecular heterolysis has been considered in terms of Winstein's scheme, according to which heterolysis takes place via the consecutive formation of a contact ion pair (CIP), a solvent-separated ion pair (SSIP), and a free carbocation [4–6, 8, 9] (Scheme 1):



$$\underset{}{\mathrm{RX}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\text{CIP}}{\mathrm{R^+X^-}} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \underset{\text{SSIP}}{\mathrm{R^+|Solv,\ Solv|X^-}} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{R^+ + X^-} \longrightarrow \text{Reaction products}$$

Scheme 1.

It is assumed that the rate constants of all steps of this process, including that of internal ion pair return (k_{-1}) and external ion pair return (k_{-2}) and, in some cases, k_{-3}, have an effect on the heterolysis rate.

Scheme 1 is virtual rather than real. It is attractive for its obviousness. It is beyond doubt that the heterolysis of a covalent bond must begin with the formation of a CIP and end in the formation of a free carbocation, proceeding via the formation of an intermediate association species of two solvated ions—SSIP. Anything that seems obvious is easily learned, but it cannot serve as evidence. Because of lack of evidence, this heterolysis mechanism has not been revised since the 1950s [10]. Winstein's scheme provides no answer for the following basic questions: Which step is the rate-limiting one? What happens in the transition state? It remains unclear how the CIP turns into the SSIP and how this process is affected by the solvent and neutral salts [11, 12].

The term *heterolysis*, which is used S_N1 and E1 reactions, implies that these reactions begin with the heterolytic dissociation of a covalent bond under the action of the solvent. This created the myth that there is nucleophilic solvent assistance (NSA) [4, 5, 13, 14], specifically, the formation of a linear quadrupole between the covalent substrate and solvent dipoles ($^{\sigma+}\mathrm{solv}^{\sigma-} \to \mathrm{R}^{\sigma+}\mathrm{X}^{\sigma-}$), which is favorable for CIP formation [14]. This how the chimerical idea of NSA appeared, and hundreds of chemists have been vainly attempting to observe this effect over the last 40 years [14–17]. However, no reliable evidence has been obtained to date for the existence of NSA in the heterolysis of not only tertiary, but also secondary and primary substrates, in which there is no steric hindrance to rear-side nucleophilic solvation [6, 11, 17].

Experiments demonstrated the rate of heterolysis of secondary substrates is independent of the nucleophilicity of the solvent. It is well describable in terms of the polarity parameter $f(\varepsilon) = \varepsilon - 1/\varepsilon + 1$ and electrophilicity parameter E or in terms of the solvatochromic parameters of the solvent ionizing power ($Z(E_T)$), which correlate satisfactorily with the polarity and electrophilicity parameters [6, 11, 12]. The following relationships are valid for 3-bromocyclohexene (**1**) and Ph_2CHBr [18]:

$$\log k_1 = -19.5 + 0.0476Z \text{ (correlation factor, } R = 0.984\text{, number of measurements, } N = 30),$$

$$\log k_{Ph_2CHBr} = -21.9 + 0.0868E_T\ (R = 0.978, N = 27),$$

$$\log k_{Ph_2CHBr} = -10.2 + 2.88f(\varepsilon) + 0.978E\ (R = 0.979,\ N = 27).$$

The rate of heterolysis of tertiary substrates, such as 2-bromo-2-methyladamantane (**2**) and cumyl chloride (**3**), decreases with an increasing solvent nucleophilicity (B) [11, 12]:

$$\log k_2 = -6.32 + 3.94f(\varepsilon) + 1.12E - 2.02B\ (R = 0.979, N = 15;\ \text{without } B \text{ taken into account, } R = 0.889),$$

$$\log k_3 = -0.362 + 0.182Z - 0.378B\ (R = 0.976, N = 10;\ \text{without } B \text{ taken into account, } R = 0.938).$$

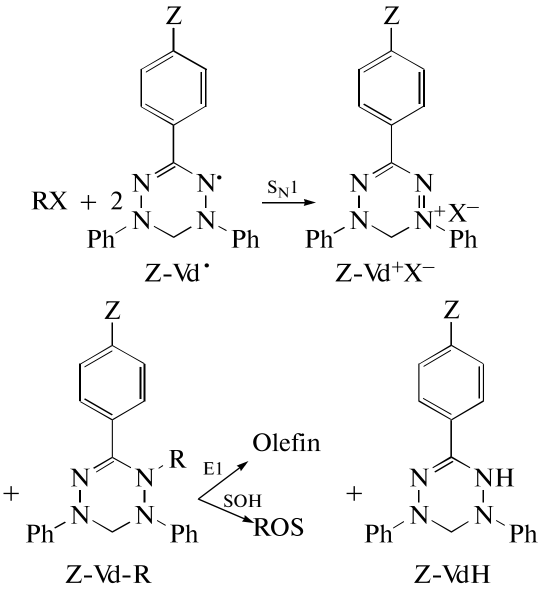
These are other examples relevant to the subject [6, 11, 12].

The solvent nucleophilicity effect on the unimolecular heterolysis rate is among the most important issues of physical organic chemistry. It has been a subject of extensive studies and incessant discussions for 70 years [5, 6, 11–18]. Some researchers believe that the solvent nucleophilicity increases the reaction rate [19–23], some researchers claim the reverse [6, 7, 11, 12, 24], and others hold that the reaction rate is independent of solvent nucleophilicity [25, 26].

The incorrect approach to the role of nucleophilicity in heterolysis reactions [13, 14. 16] has led to the revival of speculative heterolysis schemes [16, 19, 22] based on the conceptions of Swain [27] and Shilov [28] concerning the donor–acceptor interaction in the transition state.

The existence of electrophilic solvent assistance is beyond doubt. By analogy with nucleophilic assistance, it is usually designated $R^{\sigma+}X^{\sigma-} \rightarrow {}^{\sigma+}solv^{\sigma-}$ [6, 11, 16]; however, it is un clear at which stage of the process it takes place.

The rate of unimolecular heterolysis is commonly determined from the variation of the concentration of the substrate or reaction products. These reaction rate measurement methods are unsuitable for slow reactions, particularly for those in aprotic solvents. We have developed and widely tested the so-called verdazyl method, in which the steady-state SSIP concentration is considered [29]. This method enables one to determine, within a few hours, the rate of heterolysis of substrates with $\tau_{1/2} \approx 200$ years and to acquire data unobtainable by other methods [6, 24, 30]. This is an indicator method. The reaction is conducted in the presence of small amounts of stable 1,3,5-triphenylverdazyl radicals (**Z-Vd**$^\bullet$), react rapidly and entirely with the SSIP of the substrate yield the verdazylium salt **Z-Vd**$^+$**X**$^-$ and the verdazyl alkylation product **Z-VdR** (S_N1 reaction). Z-VdR decomposes rapidly via an E1 reaction into an olefin and a leucoverdazyl (**Z-VdH**). The solvolysis of Z-VdR yields Z-VdH and the solvolysis product **ROS**. The reaction takes place according to the stoichiometric equation



$Z = OCH_3, CH_3, H, Cl, NO_2.$

The rate of the reaction is monitored spectrophotometrically as the decrease in the Z-Vd$^\bullet$ concentration ($\lambda_{max} \approx 720$ nm) and/or as the formation of Z-Vd$^+$X$^-$ ($\lambda_{max} \approx 540$ nm):

$$w = -d\left[Z - Vd^\bullet\right]/2dt = d\left[Z - Vd^+X^-\right]/dt = k[RX].$$

Verdazyl is practically nonreactive toward the CIP [31]. The formation of an equimolar mixture of Z-Vd$^+$X$^-$ and Z-VdH via the E1 and solvolysis reactions is proved by comproportionation (reaction opposite to disproportionation) occurring in the system [32]:

$$Z\text{-}Vd^+X^- + Z\text{-}VdH + NaOH \rightarrow 2Z\text{-}Vd^\bullet + NaX + H_2O.$$

The rate constants determined by the verdazyl method are in good agreement with those determined by other methods. This has been demonstrated by 30 examples (20 substrates and 15 solvents) [6, 24, 29] and is illustrated in Fig. 1 [11]. Over 80% of the salt and solvation effect data available from the literature were obtained by the verdazyl method [6, 7, 11, 12, 24, 29].

The covalent bond heterolysis mechanism is usually considered in terms of a simple scheme in which an intermediate Int initially forms via a reversible process and then the intermediate turns into the reaction products [4, 5, 13–17]:

$$\text{RX} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{Int} \xrightarrow{k_2} \text{Reaction products.}$$

In this case, $k = k_1k_2/(k_{-1} + k_2)$. If the rate-limiting step is Int formation, then $k = k_1$. If the rate-limiting step is the formation of the reaction products, then $k = Kk_2$, where $K = k_1/k_{-1}$. In both cases, the constant k has dimensions of s^{-1} [33]. The lifetime of the transition state or Int, whose energy is close to that of the SSIP transition state, is known to be the inverse of the first-order rate constant: $\tau = 1/k$ [33, 34]. Eremin in his monograph [33] wrote, "This relationship is very important, for it provides a better understanding of the physical meaning of the first-order rate constant." This relationship between k and τ is used in transition state theory [2, 33, 35]. For example, it is assumed that the conversion of the activated complex into reaction products is a first-order reaction whose rate constant is $k^{\#} = 1/\tau$. If the unit of measure of k is s^{-1}, then the lifetime of Int in t-BuCl heterolysis in n-BuOH and $PhNO_2$ at 25°C is approximately 1 and 200 years, respectively [7]—complete nonsense.

The lifetime of the transition state, which is equal to the oscillation period of the molecule in the solvent cage, is known to be 10^{-13} s [35, 36], and the lifetime of cationoid intermediates is on the order of nanoseconds or picoseconds [37]. The $\tau = 1/k$ relationship is conventionally formulated as follows: the inverse of any first-order rate constant is equal to the mean lifetime of the reacting molecules [33–35]. This formulation suffers from some ambiguity: the reacting molecule may be understood as a covalent substrate. However, the $1/k$ ratio in this case has no physical meaning since it is merely close to the half-life of the substrate, $\tau_{1/2} = 0.693/k$. For correct use of the $\tau = 1/k$ relationship, it is necessary to consider the heterolysis mechanism in detail.

New facts demonstrate that Winstein's scheme is based on gross interpretation errors, specifically, on the misinterpretation of the special salt effect, the so-called salt effect due to the law of mass action [38], and the effect of solvent nucleophilicity on the heterolysis rate [6, 11, 12]. It was established that the special salt effect is due the action of the salt on the CIP, not SSIP [38, 39]. This was confirmed by picosecond spectroscopy [40]. We demonstrated in an earlier work [41] that the salt effect due to the law of mass action is associated with the action of the salt or its ions on the SSIP.

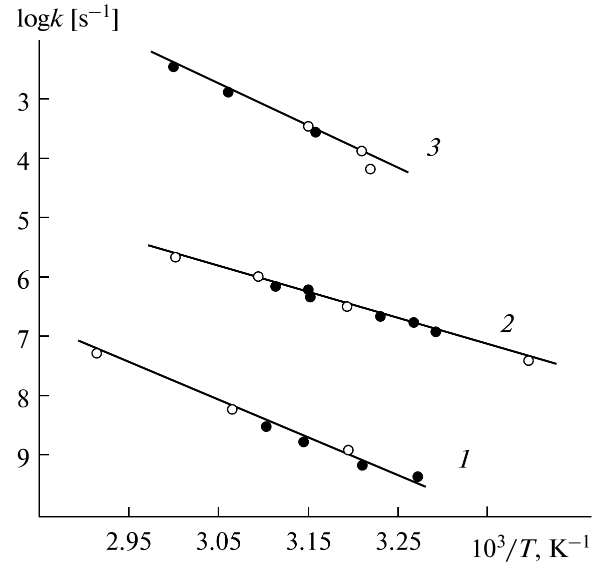


Fig. 1. log$k$ versus $1/T$ for the heterolysis of (*1*) t-BuCl in $PhNO_2$, (*2*) t-BuBr in acetone, and (*3*) 1-AdOPic in sulfolane. The black points refer to the verdazyl method; the open circles, to other methods.

Figure 2 shows the kinetic curves of 1,1-dimethylallyl chloride (**4**) heterolysis in ethyl acetate in the presence of $\text{H-Vd}^\bullet$ (E1 reaction) at 40.6, 52.1, and 56.0°C [42]:

$$CH_2{=}CHC(CH_3)_2Cl + 2\text{H-Vd}^\bullet$$
$$\to CH_2{=}CHC(CH_3){=}CH_2 + \text{H-Vd}^+Cl^- + \text{H-VdH}.$$

Here, the substrate conversion is ~0.002% and the $\text{H-Vd}^\bullet$ conversion is ~10%. The kinetic curves of the heterolysis of chloride **4** consist of two linear portions. Therefore, the reaction proceeds according to the steady-state concentration principle. Each run begins with a short induction period associated with the passage of the reaction system to the steady state, $RX \to R^+X^-$. It is assumed that, at $[RX] \gg [R^+X^-]$, [CIP] = const. This process, which is likely due to intramolecular electron transfer, would be expected to occur very rapidly. However, Fig. 2 indicates that this process is fairly slow and, as the temperature is lowered from 56 to 40°C, the induction period increases from 15 to 30 min. This is due to the solvent and substrate containing microimpurities that exert no significant on the heterolysis rate but slow down the passage of the reaction system to the steady state by CIP interception. After multiple purifications of the reactants, the induction period is much shorter and is almost unobservable, and its existence is indicated only by the fact that extrapolation of the second portion of the kinetic curve to the zero time leads to an $\text{H-Vd}^\bullet_{\text{extr}}$ concentration exceeding the initial $\text{H-Vd}^\bullet$ concentration. After the induction period, the $\text{H-Vd}^\bullet$ concentration changes linearly, obeying the zeroth-order rate equation $w = k_0$. From the slope of the $[\text{H-Vd}^\bullet]$ versus time line, it is possible to determine the constant k_0: $k = k_0/[RX]$. The rate of heterolysis of chloride **4** has been determined for 17 solvents [42]. It is satisfactorily

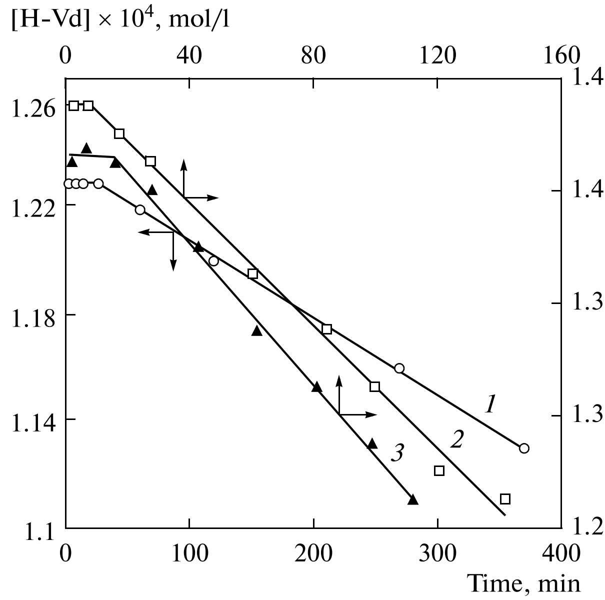
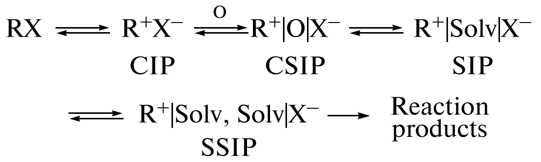


Fig. 2. Heterolysis kinetics of 1,1-dimethylallyl chloride (**4**) in ethyl acetate in the presence of 1,3,5-triphenylverdazyl (H-Vd$^\bullet$): (*1*) [**4**] = 0.737 mol/l, 40.6°C, $k = 3.16 \times 10^{-10}$ s^{-1}, $\tau = 3.2 \times 10^{-10}$ s; (*2*) [**4**] = 0.695 mol/l, 52.1°C, $k = 1.35 \times 10^{-9}$ s^{-1}, $\tau = 1.4 \times 10^{-9}$ s; (*3*) [**4**] = 0.618 mol/l, 56.0°C, $k = 1.78 \times 10^{-9}$ s^{-1}, $\tau = 1.8 \times 10^{-9}$ s.

describable in terms of the polarity parameter $f(\varepsilon)$, electrophilicity parameter E, and cohesion parameter δ^2: $\log k_4 = -12.3 + 2.83f(\varepsilon) + 0.0653E + 0.322\ \delta^2$ ($R = 0.960$, $N = 17$). At 25°C, $k = 1.6 \times 10^{-10}$ s^{-1}. The linearity of the second portion of the kinetic curve suggests that the CIP concentration is invariable during the kinetic experiment. It was indeed demonstrated that Z-Vd$^\bullet$ reacts not with the CIP, but with the later intermediate SSIP [11]. Therefore, the variation of the concentration of Z-Vd$^\bullet$, which plays the role of a scavenger, is a measure of the number of RX molecules that have reacted at a given substrate concentration, so $dN/d\tau = kN$, where N is the number of substrate molecules in 1 cm^3 of the reaction system. Since the process rate in the case considered is time-independent, $dN/d\tau = kN$, where dN is the number of reacted substrate molecules that have reached the transition state and have a lifetime sufficiently long for subsequent interaction with Z-Vd$^\bullet$ or another nucleophile. Therefore, under steady-state Int concentration conditions, k has dimensions of l/mol rather than s^{-1}, for k_0 is a dimensionless quantity because of $dx/dt = 0$ [33–35]. Accordingly, the heterolysis rate depends only on the steady-state CIP concentration.

According to the latest data [6, 11, 12, 24, 30, 38], unimolecular heterolysis proceeds via the consecutive formation of the following four types of ion pairs: CIP, cavity-separated ion pair (CSIP), solvent-shared ion pair (SIP), and SSIP (Scheme 2). The free carbocation forms only in water or in water-rich aqueous solutions [9].



$$\mathrm{RX} \rightleftharpoons \underset{\mathrm{CIP}}{\mathrm{R^+X^-}} \xrightleftharpoons{\mathrm{o}} \underset{\mathrm{CSIP}}{\mathrm{R^+|O|X^-}} \rightleftharpoons \underset{\mathrm{SIP}}{\mathrm{R^+|Solv|X^-}}$$

$$\rightleftharpoons \underset{\mathrm{SSIP}}{\mathrm{R^+|Solv,\ Solv|X^-}} \longrightarrow \begin{array}{c}\text{Reaction}\\ \text{products}\end{array}$$

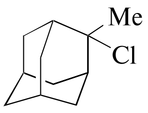
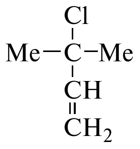
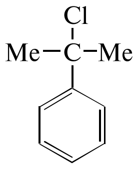
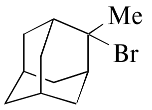
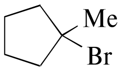
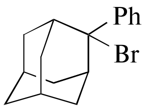
Scheme 2.

The absence of NSA suggests that the CSIP forms after the rate-limiting step and that the adverse nucleophilic solvation effect is due to CIP solvation before the rate-limiting step. This stabilizes the intermediate and complicates ion separation in the transition state. It was demonstrated [43, 44] that the nucleophilic solvation of the CIP makes difficult nucleophuge removal via the S_N1 mechanism.

The first step yields a CIP via intramolecular electron transfer from a molecular orbital of the covalent substrate to an orbital of the nucleophuge at a rate nearly equal to the speed of light. The resulting ion pair is stabilized via the formation of a coordination complex with a solvent molecule, $^{\sigma+}\mathrm{solv}^{\sigma-} \rightarrow \mathrm{R^+X^-}$. The formation of the coordination complex in the heterolysis of tertiary substrates needs steric hindrance to be overcome, and this is the cause of the adverse effect of nucleophilic solvation [45]. There is stereochemical evidence for the formation of such complexes. For example, the products of the solvolysis of optically active secondary substrates in the presence of acetone, Bu_2O, RCN, and the like partially or completely retain the configuration of the initial substrate [46, 47]. The formation of the coordination complex is accompanied by the structuring of the solvent around the cationoid. This is favorable for the formation of a primary solvation shell, which makes the lifetime of the complex sufficiently long for this complex to encounter a solvent cavity. This takes place in the cybotactic region at a rate of 10^{11}–10^{13} s^{-1} [48, 49], which is 2–3 orders of magnitude higher than the diffusion rate (5×10^9 l mol^{-1} s^{-1}) [49]. Therefore, the CIP forms without NSA.

In the rate-limiting step, the CIP solvate interacts with a solvent cavity (**o**). The cavities account for ~10% of the volume of the liquid [50]. They result from liquid density fluctuations and "move" in the solution with a velocity equal to the diffusion rate [51]. The interaction between the CIP and the solvent cavity is accompanied by the partial desolvation of the intermediate. This yields a CSIP, which turns into an SIP at a rate exceeding the diffusion rate by a factor of 100. The SIP turns equally rapidly into an SSIP. Both of these intermediates react rapidly and quantitatively with Z-Vd$^\bullet$ or another nucleophile [11].

The formation of a coordination complex of CIP in the heterolysis reaction in γ-butyrolactone is confirmed by the observation of transition state isoentropicity, $\Delta S^{\#}$ = const [52]. Below, we illustrate the isoentropicity phenomenon observed in the heterolysis of *t*-BuCl, 2-methyl-2-chloroadamantane, chloride **4**, benzhydryl bromide, *t*-BuBr, chloride **3**, bromide **2**, 1-bromo-1-methylcyclopentane, and 2-beromo-2-phenyladamantane:

	t-BuCl		$\mathrm{Me{-}C(Cl)(Me){-}CH{=}CH_2}$	Ph_2CHBr	*t*-BuBr				
$-\log k_{25}$ [s^{-1}]	8.6	7.0	6.4	5.7	5.6	5.4	4.0	3.8	3.4
$\Delta H^{\#}$, kJ/mol	101	95	88	87	86	82	79	72	74
$-\Delta S^{\#}$, J mol^{-1} K^{-1}	72	60	73	64	65	72	60	73	60

In this substrate series, the heterolysis rate constant increases by 5 orders of magnitude, while $\Delta S^{\#}$ varies only within the experimental error: $-\Delta S^{\#} = 66 \pm 6$ J mol^{-1} K^{-1} [52].

This isoentropicity is evidence that the substrates are solvated in γ-butyrolactone in the same way. This can be the case only for the CIPs, not for the covalent substrates themselves, because the rear-side nucleophilic solvation of the adamantyl substrates is impossible.

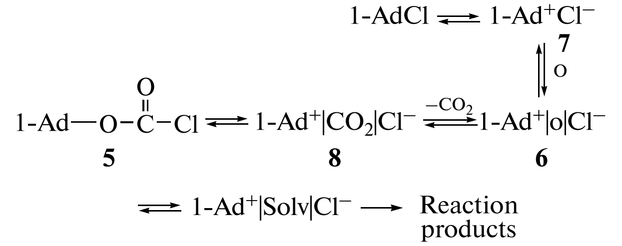
Desolvation occurring in the transition state is indicated by the isoenthalpicity observed in heterolysis reactions in γ-butyrolactone [52]. As $\Delta S^{\#}$ grows at a nearly constant enthalpy of $\Delta H^{\#} = 115 \pm 1$ kJ/mol, the reaction rate increases by more than 4 orders of magnitude:

	PhCHClMe	1-AdI	1-AdOTs	1-AdOPic
$-\log k_{25}$ [s^{-1}]	9.0	7.9	6.1	4.7
$\Delta H^{\#}$, kJ/mol	115	116	114	116
$-\Delta S^{\#}$, J mol^{-1} K^{-1}	−34	−17	+19	+54

In this substrate series, the heterolysis rate depends only on the nature of the nucleophuge and decreases with an increasing degree of solvation. This is in conflict with the well-known fact that the electrophilic solvation of a nucleophuge favors heterolysis. The increase in the heterolysis rate with an increasing degree of desolvation of the nucleophuge suggests that, in this case, the determining factor in the reaction rate is the second step of the process, in which the CIP solvate interacts with a solvent cavity, which is accompanied by the partial desolvation of the cationoid.

Figure 3 plots $\Delta H^{\#}$ versus $\Delta S^{\#}$ for the heterolysis of 13 substrates in γ-butyrolactone. Clearly, there are two distinct linear dependences, one isoentropic (A) and the other isoenthalpic (B).

One of the proofs for intermediate CSIP formation is the fact that the S_N1 and F1 reactions yield the same intermediate [53]. For example, in the heterolysis of 1-AdCl (S_N1 reaction) and 1-adamantyl chloroformate (F1 reaction), the only possible intermediate is CSIP **6**, which results from the interaction between CIP **7** and a solvent cavity. The same ion pair results from the fragmentation of CIP **8** separated by a neutral molecule [54]:



The rate of heterolysis of chloroformate **5** in seven different solvents (MeOH, EtOH, 2-PrOH, *t*-BuOH, $PhNO_2$, MeCN, and *n*-decane) is described well by the Kirkwood function [54]:

$$\log k_5 = -1.48 + 24.7 f(\varepsilon) \quad (R = 0.978, N = 7).$$

The rate of this reaction is independent of solvent polarity. On passing from $PhNO_2$ to EtOH, whose polarities are similar, the *t*-BuCl and 1-AdOTs heterolysis rates increase by 3 orders of magnitude as a consequence of the H-coordination of the nucleophuge, while the chloroformate **5** heterolysis rate remains practically invariable. These data are in good agreement with Scheme 2, suggesting that the CIP initially forms and only then undergoes solvation.

There are other proofs of the intermediate formation of the CSIP. A quantum chemical analysis of the separation of oppositely charged ions in a liquid lead to the conclusion that the conversion of the CIP into the SSIP occurs in two steps: initially, the ions of the CIP move apart to become a "CIP that has begun to separate," and then a solvent molecule enters the interion space [55, 56]. Monte Carlo simulation of *t*-BuCl heterolysis demonstrated that nucleophilic attack on the CIP begins no sooner than the ions are separated by a distance of ~5 Å [57]. Therefore, the conversion of the CIP into the SSIP includes the above-described

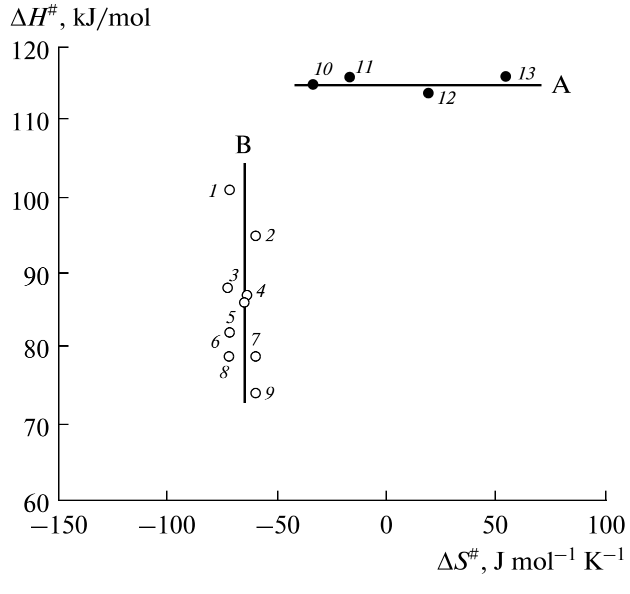


Fig. 3. $\Delta H^{\#}$ versus $\Delta S^{\#}$ for the heterolysis of a number of substrates in γ-butyrolactoneat 25°C: (*1*) *t*-BuCl, (*2*) 2-methyl-2-chloroadamantane, (*3*) 1,1-dimethylallyl chloride, (*4*) Ph_2CHBr, (*5*) *t*-BuBr, (*6*) cumyl chloride, (*7*) 2-bromo-2-methyladamantane, (*8*) 1-bromo-1-methylcyclopentane, (*9*) 2-bromo-2-phenyladamantane, (*10*) PhCHClMe, (*11*) 1-AdI, (*12*) 1-AdOTs, and (*13*) 1-AdOPic.

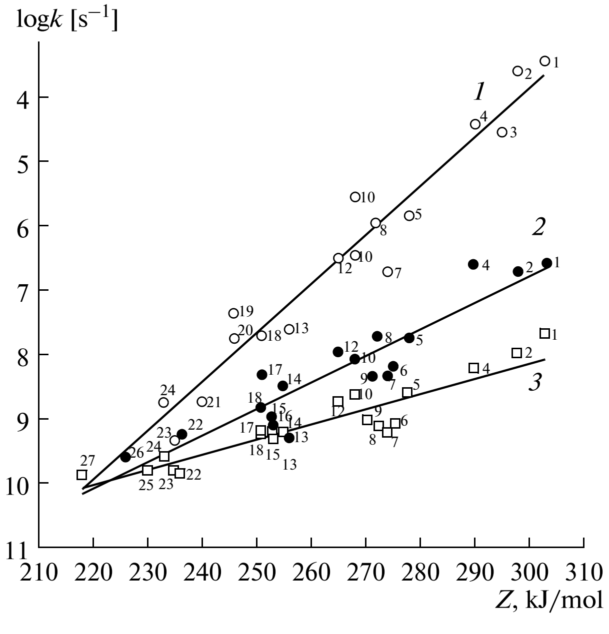


Fig. 4. log*k* versus the ionizing power *Z* of the solvent for the heterolysis of (*1*) *p*-methoxybenzotrichloride, (*2*) 1-methyl-1-chlorocyclopentane, and (*3*) 1-methyl-1-chlorocyclohexane at 25°C in aprotic solvents: (1) propylene carbonate, (2) MeCN, (3) sulfolane, (4) γ-butyrolactone, (5) $PhNO_2$, (6) acetone, (7) PhCOMe, (8) PhCN, (9) cyclohexanone, (10) EtCOMe, (11) MeCOOEt, (12) 1,2-dichloroethane, (13) PhCOOEt, (14) PhI, (15) PhBr, (16) PhCl, (17) PhOMe, (18) *o*-dichlorobenzene, (19) THF, (20) PhOEt, (21) Ph_2O, (22) Et_2O, (23) *o*-xylene, (24) PhMe, (25) *p*-xylene, (26) C_6H_6, and (27) cyclohexane.

two steps. This inference is in good agreement with the hole structure of the liquid [50, 58].

Investigation of the heterolysis kinetics by novel methods, namely, the verdazyl technique and picosecond spectroscopy [57, 59–61] has substantially widened the experimental opportunities, has provided a deeper insight into the mechanism of the process, and has eliminated the accumulated contradictions [6, 11, 24, 38].

The verdazyl method has made it possible to thoroughly study the aprotic solvent effect on the heterolysis rate. It was demonstrated that, under nonspecific solvation conditions (in cyclohexane), the heterolysis rate is independent of the nature of the substrate, with $\Delta G^{\#}$ = constant (table) [11, 62]. This finding was explained by the existence of a threshold effect, which is due to the fact that the CIP lifetime is practically independent of the substrate structure. The table presents heterolysis rate data for 19 substrates in cyclohexane and MeCN. In MeCN, a polar solvent, the heterolysis rate varies over a range of 6 orders of magnitude; in cyclohexane, in which there is no specific solvation, it does not depend on the substrate structure ($\log k_{25} = -10.0 \pm 0.3$ [s^{-1}]). This value received the name of the universal minimum heterolysis rate constant [11, 62]. The dependence of the heterolysis rate constant on the ionizing power of the solvent is plotted in Fig. 4. This dependence can be considered as a particular case of the isokinetic dependence—isoenergetic relationship [12, 35].

It was established in 1984 [63, 64] that the rate constant of CIP dissociation (CIP → SSIP), which is often treated as a diffusion-controlled process, is $k_1 = 1.6 \times 10^{10}\,s^{-1}$ in 50% aqueous CF_3CH_2OH. This value was obtained by dividing the diffusion rate constant (k_D) by the dissociation constant of two oppositely charged ions. The rate constant of diffusion in solution, derived from the rate of the reaction of N_3^- with free carbocations, is $k_D = (5–7) \times 10^9\,l\,mol^{-1}\,s^{-1}$ [63]. Calculation of the diffusion rate from the rate ofπ-dimerization between the anthracene cation and anthracene molecule yields a value of ~$1.5 \times 10^{10}\,l\,mol^{-1}\,s^{-1}$ [35, 65], which is 2–3 times larger than the value reported by Richard et al. [63]. This is likely due to the fact that the CIP–solvent cavity interaction was ignored in that study.

Direct determination of the rate constant of the CIP → SSIP reaction by picosecond spectroscopy revealed that this rate constant depends only slightly on the substrate structure and the nature of the solvent and that its value is on the order of $10^{10}\,s^{-1}$ [59–61]. For Ph_2CHCl heterolysis in MeCN at 23°C, $k_1 = 3.6 \times 10^9\,s^{-1}$ [66]; for the same process in CF_3CH_2OH, $k_1 = 3.9 \times 10^9\,s^{-1}$. For 3-methoxybenzhydryl chloride heterolysis, $k_1 = 1.1 \times 10^{10}\,s^{-1}$; for 3-methoxy-3'-methylbenzhydryl acetate heterolysis, $k_1 = 2.3 \times 10^{10}\,s^{-1}$ [60].

Rate constants of the heterolysis of various substrates in cyclohexane and acetonitrile at 25°C[a]

Substrate	$-\log k_{25}$ [s^{-1}]	
	Cyclohexane	Acetonitrile
PhCHClMe	10.2	9.11
t-BuCl	10.0[b]	8.64
1-Methyl-1-chlorocyclohexane	10.1 (9.88)[c]	7.98
1-Methyl-1-chlorocyclopentane	10.3 (9.87)[c]	6.70
CH_2=CH-CMe_2Cl	10.4	6.56
Ph_2CCl_2	9.80	5.58
2-Phenyl-2-chloroadamantane	9.80[d]	5.77
1-AdOTs	9.60	5.71
1-Bromo-1-methylcyclohexane	9.81 (9.56)[c]	6.01
Ph_2CHBr	9.80	5.60
t-BuBr	10.4	5.90
3-Bromocyclohexene	9.60	5.59
$PhCMe_2Cl$	10.4	5.30
1-AdOPic	10.0	4.91
α-Chlorobenzyl methyl ether	10.2	4.54
p-Methoxybenzotrichloride	10.4 (9.83)[b]	3.59
7α-Bromocholesterol benzoate	9.70 (9.54)[b]	3.62
2-Bromo-2-methyladamantane	9.70 (9.37)[b]	4.07
1-AdOCOCl	10.1[e] (10.1)[f]	3.15
Average	10.0 ± 0.3	

[a] The a-chlorobenzyl methyl ether heterolysis rate constants were determined by NMR spectroscopy [74]; the other data wereobtained by the verdazyl method through extrapolation of $\log k$ as a function of $Z(E_T)$.

[b] Average value for *t*-BuCl heterolysis in 11 aprotic solvents ($PhNO_2$, PhCN, acetone, PhCOMe, cyclohexanone, 1,2-dichloroethane, CH_2Cl_2, $CHCl_3$, dioxane, Et_2O, *t*-BuCl).

[c] The number in parentheses is the value obtained by extrapolation of $\log k$ as a function of $1/T$.

[d] Calculated from the relationship $\log k = -12.1 + 5.72\pi^* + 10.7\alpha$ ($R = 0.963$, $S = 0.30$, $N = 5$).

[e] Determined by extrapolation of $\log k$ as a function of $f(\mathrm{e})$.

[f] Determined directly by the vendazyl method in *n*-decane.

The verdazyl method and picosecond spectroscopy lead to very different rate constant values (10^{-10} and 10^{10} s^{-1}, respectively), whose dimensions are the same, however. This may be due to the fact that these methods probe different aspects of the process. The CIP-to-SSIP conversion rate is determined in both cases, but either method is associated with its own way of CIP formation. In the verdazyl method, the CIP forms via the mechanism presented in Scheme 2. In picosecond spectroscopy, it forms from the radical pair resulting from irradiation of a substrate solution with 266-nm light in a picosecond laser device [67, 68]. The error of rate constant determination is generally 10–20%, and sometimes it is as large as 50%. The CIP that forms under the verdazyl method conditions in a thermal regime is stabilized by solvation. Accordingly, the heterolysis rate in this case depends strongly on the nature of the solvent and can vary over a range of ~10 orders of magnitude. For example, the rate of *t*-BuCl heterolysis in water is 9 orders of magnitude higher that the rate of the same process in cyclohexane [7]. The CIP generated in a picosecond laser spectrometer likely does not undergo solvation. This is indicated by the weak dependence of the rate constant on the nature of the solvent. Therefore, CIP solvation cannot be the cause of the discrepancy between k and k_1. Hence, this discrepancy should be attributed to the difference between the dimensions of the constants. The dimensions of k_1, the constant measured by picosecond spectroscopy, are undoubtedly s^{-1}, because the process rate in this case is derived from the variation of the CIP and/or SSIP concentration. A different situation takes place when the verdazyl method is used. According to the heterolysis mechanism presented in Scheme 2, the quantity measured by the verdazyl method is actually the steady-state SSIP concentration, which depends only on the CIP concentration. The latter takes a steady-state value under the condition that $[\mathrm{RX}] \gg [\mathrm{R}^+\mathrm{X}^-]$. For example, in *t*-BuCl heterolysis in $PhNO_2$, the steady-state conditions persist over more than 500 years, so it is pertinent to assume that, in our case, $\Delta t = 0$ and the rate constant k has dimensions of l/mol. In view of the relationship $\tau = 1/k_1$, the rate constant of formation of the transition state in cyclohexane is 10^{10} s^{-1} and the lifetime of the transition state is 10^{-10} s. The validity of the $\tau = 1/k_1$ relationship in our case is suggested by the fact that the rate of both reactions is diffusion-controlled ($k_D \approx 10^{10}$ l mol^{-1} s^{-1}). However, k has dimensions of s^{-1}.

According to Scheme 2, the SSIP results from the interaction between the CIP and a solvent cavity. The cavity appears owing to diffusion, whose rate constant has dimensions of l mol^{-1} s^{-1}. In view of this, k should have dimensions of l mol^{-1}/l mol^{-1} s^{-1} = s. These are the dimensions of the rate constant of the bimolecular interaction between the CIP solvate and a solvent cavity. Therefore, $k = k_D/K$, where K is the CIP formation equilibrium constant. This relationship was used to calculate the CIP-to-SSIP conversion rate constant: $k_1 = 1.6 \times 10^{10}$ s^{-1} [63, 64]. According to our data for 19 substrates (table), the average k_1 value is ~10^{10} s^{-1}; for the three substrates for which the rate constant is derived from $\log k$ as a function of $1/T$ (p-methoxybenzotrichloride, 1-methyl-1-chlorocyclopentane, and 1-methyl-1-chlorocyclohexane), $k_1 = 1.3 \times 10^{10}$ s^{-1}. The rate constants determined by the verdazyl method are in good agreement with the values determined by measuring the substrate or reaction product concentration [6, 12, 24, 69]; therefore, in all cases, the constant in the equation $w = k$[RX] should be expressed in terms of seconds. This means that we actually measure the Int lifetime rather than the reaction rate. We came to this conclusion in an earlier study, based on the fact that the minimum t-BuCl heterolysis rate constant (10^{-10} s^{-1}) is independent of the nature of the solvent in the E_T = 130–180 kJ/mol range (see Note b to the table). Assuming that the heterolysis rate constant in the $w = k$[RX] equation has dimensions of s^{-1}, we obtain the following absurd result: the rate of the limiting step, CIP → SSIP, is 10 orders of magnitude higher than the heterolysis rate.

In view of the $\tau = 1/k_1$ relationship, under nonspecific solvation conditions (in cyclohexane) the CIP dissociation rate is 10^{10} c^{-1} and the SSIP lifetime is 10^{-10} s. If this relationship is valid under specific solvation conditions, the SSIP lifetime will increase with an increasing ionizing power of the solvent (***Z***) and the CIP dissociation rate will decrease. For t-BuCl, these changes will be as large as 9 orders of magnitude. These changes are due to the fact that, on the one hand, the solvation of the CIP extends its lifetime and thus raises the probability of its encounter with a solvent cavity and, on the other hand, solvation hinders the interaction between the CIP solvate and the solvent cavity and thus makes necessary desolvation. It is commonly believed that the larger the Z value, the higher the heterolysis rate, and it is meant that it is the covalent substrate that undergoes solvation. However, the opposite trend can be observed in CIP solvation.

Since the lifetime of Int is inversely proportional to the heterolysis rate, for the heterolysis of low-reactive substrates, which form a strongly solvated, unstable intermediate Int, it is expected that the limiting heterolysis rate will be reached rapidly even in polar solvents. This assumption can be verified by examining the following substrates and correlating the rate of their heterolysis in EtOH with the Z value at which the minimum rate constant of ~10^{-10} c^{-1} is reached [6, 70–73]:

Substrate	$PhCMe_2Cl$	$CH_2{=}CHCMe_2Cl$	t-BuCl	1-AdI	1-AdCl
$-\log k$ [s^{-1}]	3.4	4.5	7.1	8.4	10.4
Z, kJ/mol	218	268	280	300	333

Therefore, CIP solvation reduces the heterolysis rate.

The conventional interpretation of the heterolysis mechanism is paradoxical in that it is reduced to discussion of the most obscure step of this mechanism. Main attention is focused on CIP formation, and the solvent electrophilicity and nucleophilicity effects on this process are discussed. Some researchers believe that the determining factor is the electrophilicity of the solvent, while others claim the existence of nucleophilic assistance or a push–pull effect of the solvent [6, 11, 12, 32, 39]. However, these hypotheses have not been corroborated by experimental data for lack of the latter. CIP formation can sometimes be detected by the verdazyl method. In Fig. 2, this process is indicated by an induction period. It is difficult to derive a certain inference from these data, because only the length of the induction period is known, which depends strongly on the presence of impurities in the substrate and solvent. By thoroughly investigating the effects of protic and aprotic solvents on the rate of heterolysis of about 30 substrates and by analyzing various isoparametric relationships, we demonstrated that the CIP formation rate is independent of the electrophilic and nucleophilic solvation effects [6, 11]. It is likely that an intramolecular electron transfer reaction (ET1) takes place here.

One of the purposes of this study was to understand why picosecond spectroscopy and the verdazyl method lead to very different rate constants in the first-order rate equation $w = k$[RX], namely, 10^{10} and 10^{-10} s^{-1}. Use of the relationship $\tau = 1/k$ for unimolecular heterolysis reactions leads to absurd results. We proposed and substantiated the hypothesis that the rate constants derived from the variation of the substrate or reaction product concentration characterize the lifetime of Int rather than the heterolysis rate. This enabled us to harmonize the first-order kinetic relationships using the $\tau = 1/k$ formula and the concept of the steady-state concentration of the intermediate.

Note that first-order reactions differ. Some of them proceed via the formation of an active intermediate Int and are described by a zeroth-order rate equation, $w = k_0$, $k = k_0/[\mathrm{RX}]$ (heterolysis, homolysis, acetone halogenation, catalytic reactions, etc.), while others take place without Int formation (radioactive decay, isomerization, dissolution in a liquid) are described by a first-order rate equation, $w = k[\mathrm{RX}]$, where k has dimensions of s^{-1}.

Thus, along with the rate constant with dimensions of s^{-1}, which is determined from the variation of the substrate or reaction product concentration, there are two fundamental constants characterizing unimolecular heterolysis reactions, namely, the rate constant of CIP dissociation or CIP conversion into SSIP via SIP interaction with a solvent cavity ($k_1 \approx 10^{10}\ \mathrm{s}^{-1}$) and the lifetime of Int in cyclohexane ($\tau \approx 10^{-10}$ s), which are interrelated as $\tau = 1/k$. When the heterolysis rate is diffusion-controlled, the identity $k_\mathrm{D} \approx k_1 = 1/\tau \approx 10^{10}\ \mathrm{s}^{-1}$ is valid.

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