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The verdazyl method for the study of the kinetics and mechanisms of the unimolecular heterolysis reactions of organic compounds

G F Dvorko, E A Ponomareva
Kiev Polytechnic Institute

ABSTRACT. **Data concerning the use of triphenylverdazyl radicals as internal indicators to study of the kinetics and mechanisms of the heterolysis of organic substrates in various protic and aprotic solvents are surveyed. The application of the verdazyl method made it possible to put forward a new mechanism of the heterolysis of a covalent bond—the reaction proceeds via the consecutive formation of contact, spatially separated, and solvent-separated ion pairs.**

The bibliography includes 135 references.

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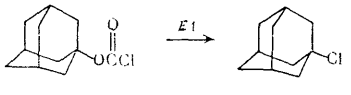
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I. Introduction

The unimolecular heterolysis reactions of organic compounds (S_N1, $E1$, $F1$, solvolysis) are widely used in laboratory and industrial synthesis.[1–3] Depending on the conditions in the heterolysis of, for example, 1-halo-1-phenylethane, one of three reactions can take place:[4,5]

$$\mathrm{PhCHXMe} \begin{cases} \xrightarrow[S_N1]{Y^-} \mathrm{PhCHYMe} + X^-, \\ \xrightarrow[E1]{} \mathrm{PhCH{=}CH_2} + \mathrm{HX}, \\ \xrightarrow[\text{solvolysis}]{ROH} \mathrm{PhCH(OR)CH_3} + \mathrm{HX}. \end{cases} \quad (1)$$

The decomposition of 1-adamantyl chloroformate may serve as an example of the fragmentation reaction:[6]



(2)

The study of the mechanism of unimolecular heterolysis reactions is in the vanguard of the mechanistic research in organic chemistry.[1,2,7,8] The mechanism of these reactions is interpreted on the basis of Winstein's ionisation-dissociation scheme (see, for example, Refs. 7–10):

$$\mathrm{RX} \rightleftharpoons \underset{\text{CIP}}{\mathrm{R^+X^-}} \rightleftharpoons \underset{\text{SSIP}}{\mathrm{R^+ \mid Solv \mid X^-}} \rightleftharpoons \mathrm{R^+ + X^-}. \quad (3)$$

It has been suggested that the reaction begins with the formation of a contact ion pair (CIP), which is then slowly converted into a solvent-separated ion pair (SSIP) and the latter rapidly decomposes, affording the free carbonium ion. The reaction products are formed from the last two intermediates. They in fact determine the type of reaction occurring. The rate of reaction is described by a first-order kinetic equation:

$$v = k[\mathrm{RX}]. \quad (4)$$

The rate increases sharply with increase in the polarity of the medium.[10–13]

The rate of the $E1$ and solvolysis reactions can be conveniently followed from the acid evolved.[14,15] The reaction is usually performed in the presence of an amine, which binds the acid and thus suppresses the reverse reaction and eliminates the possible catalytic effects of the acid. However, in an aprotic medium, the salt formed can lead to appreciable errors in the determination of the reaction rate.[16,17] The rate of the solvolysis reaction is relatively insensitive to the action of salts.[7] In a number of instances, this is true also of the $E1$ reactions.[7,11] The above method for the study of the kinetics of such reactions therefore generally yields satisfactory results.

The rates of S_N1 reactions in an aprotic medium depend greatly on the added salts,[18] which makes it difficult to obtain reliable results. The kinetics of these reactions are usually investigated by measuring the rate of the radioactive exchange of the nucleofugal species in the substrate[19] or by carrying out the reaction in the presence of strong nucleophiles (PhONa[20]). However, these methods are complex to carry out and are insufficiently correct owing to the influence of the salts present in the solution. The latter complicates the interpretation of the experiment and sometimes leads to gross errors.[20,21]

Before the appearance of the verdazyl method for the study of the unimolecular heterolysis reactions,[18,22] there was no effective method available in the literature for the study of the kinetics of S_N1 reactions in an aprotic medium. In certain cases (in polar aprotic solvents), the problem was solved by determining the rate of reaction in the presence of small amounts of water,[23,24] i.e. in a sense the rate of solvolysis was determined. However, it is noteworthy that, in order to obtain reliable results, it is necessary in this instance to carry out special investigations of the influence of water on the rate of reaction.

The interpretation of the mechanism of the *Fl* reactions occurring via an ionisation-fragmentation pathway frequently gives rise to difficulties[25,26] owing to the presence in this instance of not only consecutive but also of parallel stages.[27]

The study of the kinetics of the heterolysis of organic substrates in aprotic solvents is significantly hindered also by the fact that such reactions are very slow. Thus the half-reaction time for t-BuCl in hexane at 25 °C is $\sim 1 \times 10^9$ years[17] and the rate of heterolysis of certain skeletal compounds is even lower, by several orders of magnitude.[7,10] The accumulation of kinetic data has therefore been slow and difficult. The detailed specification of the mechanism stopped at the level of Winstein's scheme, which was proposed as early as the middle 1950s.[9,28] Attention was concentrated on the study of the solvolysis reactions, which, however, yield inadequate information since the kinetic relations for them are indefinite, the solvation effects are uniform, and the salt effects are indistinct.

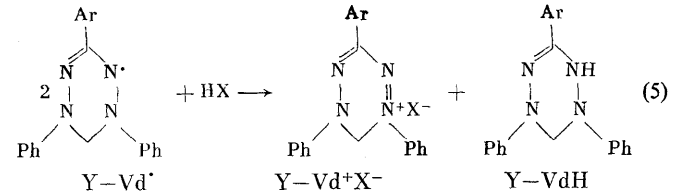
Considerable progress in the study of the kinetics and mechanism of the unimolecular heterolysis reactions was achieved by virtue of the development and wide scale application of the verdazyl method,[18,21,22,27,29–80] which uses triphenylverdazyl radicals as internal indicators. The indicator methods had been used earlier only for the study of solvolysis reactions,[81,82] but since they had no significant advantages they were not applied on a wide scale.

II. The verdazyl method for the study of the kinetics of the heterolysis of organic compounds

The application of triphenylverdazyl radicals as internal indicators in the determination of the rate of heterolysis of organic compounds is based on the fact that they react rapidly and quantitatively with the reaction products (acids[83]) or the cationoid intermediate derived from the substrate, formed after the rate-limiting stage, which makes it possible to follow the rate of reaction from the consumption of triphenylverdazyl (Y—Vd$^{\cdot}$) and/or from the formation of the verdazyl salt (Y—Vd$^+$X$^-$).

Triphenylverdazyl radicals are some of the most stable free radicals.[84] They can be readily synthesised and purified. They can be stored in air in the crystalline state for more than 10 years without appreciable changes. A solution of Y—Vd$^{\cdot}$ in non-polar solvents is stable for several days and in polar solvents for ~ 10 h.

Triphenylverdazyls react rapidly and quantitatively with hydrogen halides and the halogens:[84,85]



(5)

$$2Y\text{—}Vd^{\cdot} + X_2 \rightarrow 2Y\text{—}Vd^+X^- . \qquad (6)$$

The reaction can be readily followed spectrophotometrically from the consumption of Y—Vd$^{\cdot}$ and the formation of Y—Vd$^+$X$^-$. By virtue of the different stoichiometries of reactions (5) and (6), it is possible to determine quantitatively the content of the halogen and the hydrogen halide when they are present jointly in the solution.

The reaction of Y—Vd$^{\cdot}$ with carboxylic acids is reversible.[86–88] In an aprotic medium, the rate of reaction is described by a third-order kinetic equation:[87]

$$v = k[Y\text{—}Vd^{\cdot}]^2[RCO_2H].$$

In aprotic solvents of low polarity, I_2 reacts with Y—Vd$^{\cdot}$ also reversibly,[89] the rate of reaction being described by a fourth-order kinetic equation:[90]

$$v = k[Y\text{—}Vd^{\cdot}]^2[I_2]^2.$$

It is necessary to take this into account in the study of the heterolysis of organoiodine compounds in a non-polar medium[89] and in the study of the influence of salts of hydriodic acid on the rate of heterolysis of organic substates.[40,49] In the reaction of Y—Vd$^{\cdot}$ with Cl_2, Br_2, hydrogen halides, and other strong acids, the reaction equilibrium is almost wholly displaced towards the products.[46]

Triphenylverdazyls are powerful electron donors,[91,92] reacting readily with Lewis acids,[93–95] tetranitromethane,[98] tetracyanoethylene,[97] iminoxyls and phenoxyls,[98] the tropylium cation,[99] and the ion pair $PhN_2^+BF_4^-$.[100] These reactions proceed via electron transfer from the radical to the electrophile and the rate of reaction is described by a second-order kinetic equation, i.e.

$$v = k[\text{electrophile}][Y\text{—}Vd],$$

and increases with the enhancement of the electron-donating properties of the substituent in the radical. Clearly the Y—Vd$^{\cdot}$ radical should also react readily with the intermediate cationoids formed in the heterolysis of an organic substrate, for example with a solvent-separated ion pair.

In the heterolysis of organic substrates in the presence of Y—Vd$^{\cdot}$, identical stoichiometric ratios are usually observed regardless of the type of reaction: 2 moles of the verdazyl radical are consumed per mole of the substrate and one mole of the verdazyl salt is formed:

$$RX + 2Y\text{—}Vd^{\cdot} \begin{cases} \xrightarrow{\text{solvolysis}} Y\text{—}Vd^+X^- + Y\text{—}VdH + ROS, \\ \xrightarrow{S_N1} Y\text{—}Vd^+X^- + Y\text{—}VdR, \\ \xrightarrow{E1} Y\text{—}Vd^+X^- + Y\text{—}VdH + \text{olefin}. \end{cases} \qquad (7)$$

Verdazyls were used for the first time to study the kinetics of the dehydrohalogenation of t-butyl halides.[22,29–36,38] Apart from 1,3,5-triphenylverdazyl (Vd$^{\cdot}$), the following radicals were also used: 3-(4-methoxyphenyl)-1,5-diphenylverdazyl (MeOVd$^{\cdot}$), 3-(4-methylphenyl-1,5-diphenylverdazyl (MeVd$^{\cdot}$), 3,5-di(4-methoxyphenyl)-1-phenylverdazyl [(MeO)$_2$Vd$^{\cdot}$], 3-(4-chlorophenyl)-1,5-diphenylverdazyl (ClVd$^{\cdot}$), and 3-(4-nitrophenyl)-1,5-diphenylverdazyl (NO_2Vd$^{\cdot}$). It was postulated that Y—Vd$^{\cdot}$ reacts with the hydrogen halide split off.[22,30–32] Leucoverdazyl, which is comparatively readily oxidised by atmospheric oxygen to verdazyl, is formed in the course of E1 and solvolysis reactions. Under the conditions of the kinetic experiment, leucoverdazyl is preserved without change over a period of ~ 8 h.

In the kinetic experiment, a solution of the verdazyl at a concentration suitable for spectrophotometric determinations ($\sim 10^{-4}$ M) is mixed with a solution of the substrate at a concentration ensuring an acceptable reaction rate (from 10^{-5} to 1 M depending on the reactivity of the substrate). The solution obtained

is placed in the thermostatted cell of the spectrophotometer and the absorption strength is measured at 720 and 540 nm. Although the values of λ_{max} for Y—Vd˙ and Y—Vd$^+$X$^-$ and their extinction coefficients depend comparatively little on the nature of the substituent and the solvent,[53,56,64,66,76] the values of λ_{max} corresponding to the given verdazyl must be used in order to obtain valid data.

In the study of the kinetics of rapid reactions, the substrate concentration during the experiment may be comparable to the concentration of Y—Vd˙ [29] or may slightly exceed it.[66] In this case, the "Y—Vd˙ (Y—Vd$^+$X$^-$) concentration—time" relation is curved and the rate of reaction in each individual experiment is calculated from the kinetic equation (4). In such experiments, the degree of conversion of the substrate can reach 100%. Cases of this kind are observed rarely because the heterolysis of organic compounds is comparatively slow. The concentration of Y—Vd˙ is usually appreciably lower than the substrate concentration (by a factor of $5-10^5$), which makes it possible to carry out reliable determinations of the rates of reaction for low and very low degrees of conversion of the substrate (0.001—5%) and thus in the course of several hours one can determine the rate of a reaction with a half period reaching 1000 years. In these experiments, the substrate concentration hardly changes during the kinetic experiment, so that in each individual experiment the rate of reaction is described by the pseudo-zero-order kinetic equation $v = k_0$, the Y—Vd˙ and Y—Vd$^+$X$^-$ concentrations varying linearly as a function of time. The first-order rate constant is calculated from the equation $k = k_0[RX]$. Thus the verdazyl method is in this case based on the determination of the initial rates of reaction.

The determination of the rate of heterolysis from the consumption of Y—Vd˙ and the formation of Y—Vd$^+$X$^-$ leads to satisfactorily concordant results, the rate of reaction being independent of the concentration of Y—Vd˙ and of the nature of the substituent in the latter. Consequently the verdazyl enters into the reaction after the rate-limiting stage.

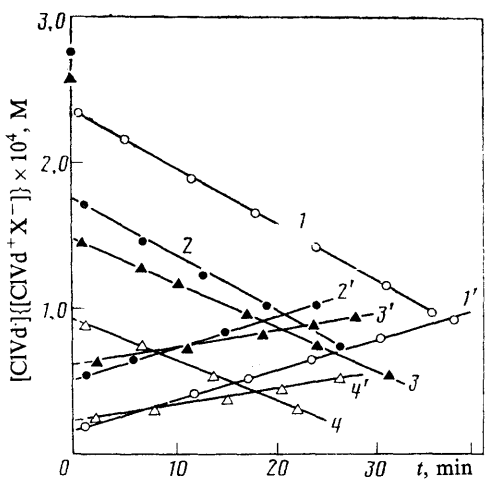


Figure 1. Kinetics of the heterolysis of t-BuBr in propylene carbonate in the presence of ClVd˙: *1*, *1'*, *2*, and *2'*, [t-BuBr] = 0.0105 M, [ClVd˙] = 2.75 × 10^{-4} M, 25 °C, k = 3.20 (3.16) × 10^{-6} s^{-1}; *3* and *3'*, [t-BuBr] = 0.025 M, [ClVd˙] = 2.60 × 10^{-4} M, 32.5 °C, k = 8.48 × 10^{-6} s^{-1}; *4* and *4'*, [t-BuBr] = 0.025 M, [ClVd˙] = 1.3 × 10^{-4} M, 32.5 °C, k = 8.67 × 10^{-6} s^{-1}.

Fig. 1 presents a series of characteristic curves for the heterolysis of t-BuBr in propylene carbonate in the presence of ClVd˙ under conditions such that [t-BuBr] ≫ [ClVd˙].[29] The ClVd˙ (straight lines *1—4*) and ClVd$^+$Br$^-$ (straight lines *1'—4'*) concentrations vary linearly with time beause the t-BuBr concentration is constant during the experiment. According to the stoichiometric Eqn. (7), the rate of reaction in each individual experiment is described by a pseudo-zero-order kinetic equation:

$$-d[Y-Vd^{\cdot}]/2dt = d[Y-Vd^+X^-]/dt = k_0. \quad (8)$$

The abrupt change in the concentrations of the radical and the salt over the initial section of the kinetic curve is caused by the rapid reaction of the radical with the hydrogen halide formed as a result of the decomposition of t-BuBr before the start of the measurements. The size of the jump increases with increase in the time interval between the preparation of the substrate solution and its mixing with the verdazyl solution. In conformity with the stoichiometry of reaction (7), on decomposition of t-BuCl the abrupt changes in the concentrations of the radical and the salt are in the ratio 2 : 1. In the case of t-BuBr and especially t-BuI, the changes in the concentrations of Y—Vd˙ and Y—Vd$^+$X$^-$ in the initial period usually differ by a factor less than 2 and in certain cases (t-BuI) the ratio is 1 : 1. This is associated with the fact that the HBr(HI) formed before the start of the measurements is fully or partly oxidised by atmospheric oxygen to the halogen.

Apart from t-butyl halides,[27,29—36,38,50,51,68,71,73] the verdazyl method has been applied to the study of *E*1 reactions involving 7α-bromocholesteryl benzoate,[59,63,64,70,74,75] 1-chloro-1-phenylethane,[60,65,69] 2-bromo-2-methyladamantane,[50,55,57,68] 2-chloro-2-methyladamantane,[71] and cumenyl chloride.[79] Similar kinetic relations were observed in all cases.

It has been shown in relation to 7α-bromocholesteryl benzoate,[70] t-BuBr,[50,68,73] t-BuCl,[68,71] cumenyl chloride,[79] 2-bromo-methyl-adamantane,[68] and 2-chloro-2-methyladamantane[68,71] that, in the course of the *E*1 reaction, the Y—Vd˙ radical reacts not with the hydrogen halide, as postulated initially, but with the solvent-separated ion pair comprising the substrate:

$$R^+|Solv|X^- + 2Y-Vd^{\cdot} \longrightarrow Y-Vd^+X^- + [Y-Vd-R] \xrightarrow{(I)} Y-VdH + \text{olefin}. \quad (9)$$

This reaction apparently results in the initial formation of the product of the alkylation of the verdazyl (I), which then decomposes comparatively rapidly into an olefin and leucoverdazyl, which agrees with the stoichiometric Eqn. (7). This conclusion was reached in the study of salt effects, which demonstrated that Y—Vd˙ and the salt act on the same cationoid intermediate.

The quantitative formation of leucoverdazyl in solution can be readily followed with the aid of the disproportionation reaction[101]

$$Y-VdH + Y-Vd^+X^- + NaOH \rightarrow 2Y-Vd^{\cdot} + NaX + H_2O. \quad (10)$$

After the addition of one drop of a 1 M aqueous NaOH solution to the reaction mixture at the end of the kinetic experiment, the initial verdazyl concentration is restored in the solution.

In contrast to t-butyl halides, 2-bromo-2-methyladamantane, and cumenyl chloride, the rate of heterolysis of 1-chloro-1-phenylethane[65,69] and especially 7α-bromocholesteryl benzoate[70,75] depends comparatively strongly on the verdazylium salt formed during the reaction, which leads to an appreciable distortion of the "Y−Vd$^{\cdot}$ (Y−Vd^{+}X^{-}) concentration−time" relation. The rate of reaction was calculated in this case from the initial linear section of the kinetic curve.

It has been shown in relation to the heterolysis of t-BuBr and t-BuCl in acetonitrile[22] and acetone,[30] of t-BuCl in isopropyl alcohol and t-butyl alcohol,[38] of PhCHClMe in ethanol,[65] and of $PhCMe_2Cl$ in acetonitrile[79] that the data obtained by the verdazyl method agree satisfactorily with the results obtained by other methods.[102−108] The gross errors made in the determination of the rate constants for the solvolysis of t-BuCl in isopropyl alcohol and t-butyl alcohol and of t-BuBr in t-butyl alcohol were detected by means of the verdazyl method. The rate constants quoted by Viana and coworkers[109,110] differ by 1−3 orders of magnitude from the values found by the verdazyl method[38] and also those quoted by Rudakov.[107]

The application of the verdazyl method proved to be particularly effective in the study of S_N1 reactions. There exist data at present on the heterolysis of Ph_2CHBr,[34,35,38−45,72] Ph_2CHCl,[21,38] 1-adamantyl iodide (1-AdI),[47,49,51] 1-AdBr,[36,48] 1-adamantyltoluene-*p*-sulphonate (1-AdOTs),[46,48,54,80] 1-adamantyl picrate (1-AdOPic),[52,53,56,80] 3-bromohomoadamantane,[58] $PhCCl_3$,[61,67,76] *p*-methoxy(trichloromethyl)benzene,[62,66] Ph_2CCl_2,[69,77] *p*-methoxybenzylidene chloride,[77,78] and di(*p*-chlorophenyl)dichloromethane.[69]

In these cases, the rate of reaction is also described by the kinetic Eqn. (4) and is as a rule independent of the concentration and nature of Y−Vd$^{\cdot}$. Consequently verdazyl enters into the reaction after the rate-limiting stage, which in fact makes it possible to use it as an internal indicator.

The rates of S_N1 reactions in an aprotic medium are very sensitive to the influence of salts, including those which are formed during the reaction. In certain cases,[40,62,68,69] the salt effect is so great that, when [Y−Vd^{+}X^{-}] ≃ 10^{-4}−10^{-5} M, the "Y−Vd$^{\cdot}$ concentration−time" relation is greatly distorted. The rate constant for the pseudo-zero-order reaction was calculated in this case either from the initial linear section of the kinetic curve, if it can be identified, or was found by extrapolating the values of k_0 or k to the [Y−Vd^{+}X^{-}] = 0 zero straight line.[62]

It has been shown in relation to the heterolysis reactions of Ph_2CHCl in methanol,[21] 1-AdOTs in isopropyl alcohol,[46] 1-AdOPic in sulpholan, methanol, and ethanol,[52,56] $PhCCl_2$ in aqueous ethanol,[76] Ph_2CCl_2 in ethanol and aqueous dioxane,[69,77] and *p*-$MeOC_6H_4CHCl_2$ in aqueous dioxane[77,78] that the rate constants found by the verdazyl method agree satisfactorily with those determined by other procedures.[24,111−117] The rate constant for the heterolysis of Ph_2CHCl in acetonitrile, found by the verdazyl method,[21] proved to be ~3 orders of magnitude lower than the value obtained in the presence of PhONa.[118] The presence of a gross error in the study of Okamoto et al.[118] has been demonstrated.[21] An even greater error was made in an investigation[119] where the rate constant for the hydrolysis of $(p\text{-}ClC_6H_4)_2CCl_2$ at 25 °C, calculated from the results of this study, proved to be ~5 orders of magnitude lower than the value found by the verdazyl method.[69]

Fig. 2 presents the temperature dependences of the logarithms of the rate constants for the heterolysis of t-BuBr in acetone[30,104] (*E*1 reaction) and of 1-AdOPic in sulpholan[52,112] (S_N1 reaction), obtained by the verdazyl method and other independent methods. In both cases, all the points lie on a single straight line, which illustrates the validity of the verdazyl method. The most convincing evidence for the validity of the method is that the enormous amount of experimental data obtained by this procedure for 21 substrates (each in 10−40 solvents) is fully consistent with the available literature data for the unimolecular heterolysis of organic compounds.

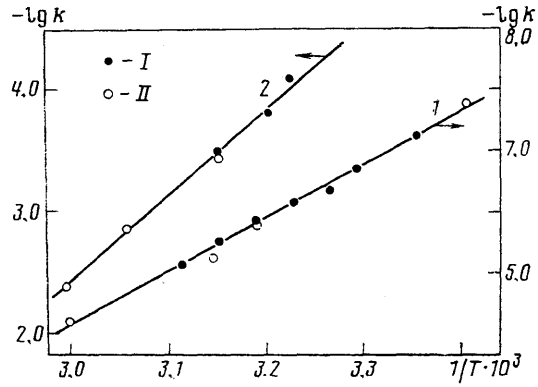


Figure 2. Temperature variation of the rate of heterolysis of t-BuBr in acetone (line *1*) and of 1-AdOPic in sulpholan (line *2*); *I*, verdazyl method; *II*, other methods.[24,104,112]

Valuable information about the mechanism of S_N1 reactions is provided by the reaction products formed with participation of verdazyl. Depending on the nature of the substrate and the reaction conditions, they can be various, different stoichiometric [RX]:[Y−Vd$^{\cdot}$]:[Y−Vd^{+}X^{-}] ratios and different forms of the kinetic pseudo-zero-order equations being observed. The verdazyl alkylation products are usually formed in the course of the reaction:[39,49,51,54]

$$RX+2Vd^{\cdot}\rightarrow Vd-R+Vd^{+}X^{-},\qquad R=Ph_2CH,\ 1\text{-}Ad. \tag{11}$$

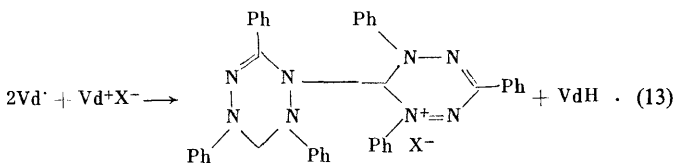
The rate of reaction is in this case described by the kinetic Eqn. (8) subject to the condition [RX] ≫ [Y−Vd$^{\cdot}$].

The solvent molecule, for example that of acetonitrile, can participate in the formation of the reaction product:[46,47,52]

$$1\text{-}AdX + 2Vd^{\cdot} \xrightarrow{MeCN} 1\text{-}Ad-N=\overset{\displaystyle Me}{\overset{|}{C}}-Vd + Vd^{+}X^{-}. \tag{12}$$

Reaction (12) indicates the intermediate formation of the ion pair 1-Ad−N=C(Me)$^{+}$X^{-}, apparently via the addition of 1-AdX to the triple bond of acetonitrile located in the interionic space of the solvent-separated ion pair 1-Ad^{+}|MeCn|X^{-}. The new ion pair formed subsequent reacts rapidly with the indicator. In this case, the kinetic relatins remain the same as in reaction (11).

The isolation of the reaction products is hindered by the occurrence of the side reaction of $Y-Vd^{\cdot}$ with $Y-Vd^{+}X^{-}$, which leads to the formation of the sparingly soluble verdazylium salt (II) and of leucoverdazyl:[26,46,47,49,52,62,120]



(II)

This rection proceeds only at comparatively high concentrations of the reactants (~0.1 M). Under the conditions of the kinetic experiment at low $Y-Vd^{\cdot}$ and $Y-Vd^{+}X^{-}$ concentrations ($\sim 1 \times 10^{4}$ M), it does not take place.[120]

In the heterolysis of polychlorinated organic compounds ($ArCCl_3$, Ph_2CCl_2, $ArCHCl_2$),[62,66,69,77,78] the verdazyl alkylation products are also apparently formed initially ($ArCl_2C-Vd$, $Ph_2ClC-Vd$, $HArClC-Vd$) and readily undergo further reactions. As a result of this, the stoichiometry of these reactions and their kinetic equations depend greatly on the nature of the substrate and the experimental conditions.

The heterolysis reaction of $PhCCl_3$ is isopropyl alcohol is described by the stoichiometric equation:

$$PhCCl_3 + 6Vd^{\cdot} \xrightarrow{iso-PrOH,\ H_2O} PhCO_2Pr-iso + 3Vd^{+}Cl^{-1} + 3VdH. \quad (14)$$

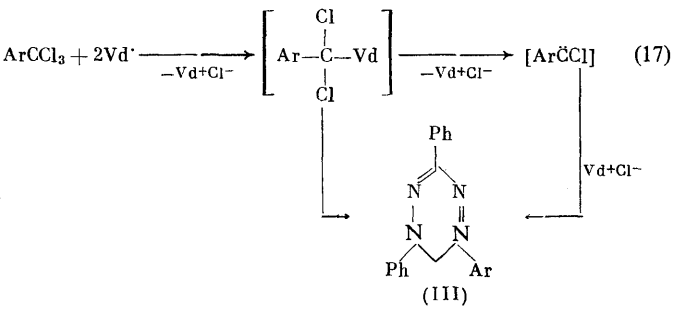
Two explanations are possible for these results. The first is that the substrate is initially solvolysed with formation of 3 moles of HCl, which then rapidly reacts with 6 moles of the indicator, while the second is that the verdazyl alkylation product formed in the first stage of the reaction is rapidly converted into $Vd^{+}Cl^{-}$ and PhCOCl and the latter is known[121] to be solvolysed ~3 orders of magnitude faster than $PhCCl_3$.[122] Regardless of the way in which this reaction takes place, it is described by the pseudo-zero-order kinetic equation

$$-d[Vd^{\cdot}]/6dt = d[Vd^{+}Cl^{-}]/3dt = k_0. \quad (15)$$

In the heterolysis of p-$MeOC_6H_4CCl_3$ in propylene carbonate, sulpholan, chloroform, and butyl acetate, the verdazyl alkylation product formed ($ArCl_2C-Vd$) is stable during the kinetic experiment and the rate of reaction in these solvents is therefore described by the pseudo-zero-order kinetic Eqn. (8).[66] In acetonitrile, γ-butyrolactone, ethyl methyl ketone, 1,1,2,2-tetrachloroethane, acetophenone, nitrobenzene, benzonitrile, and methylene chloride, the above product decomposes rapidly during the kinetic experiment with formation of $Vd^{+}Cl^{-}$. The rate of reaction in these solvents is therefore described by the pseudo-zero-order kinetic equation[62,66,76]

$$-d[Vd^{\cdot}]/2dt = d[Vd^{+}Cl^{-}]/2dt = k_0. \quad (16)$$

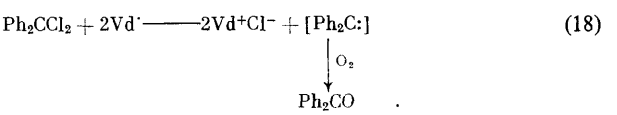
In preparative experiments carried out with $PhCCl_3$, p-$MeOC_6H_4CCl_3$, and p-$MeC_6H_4CCl_3$ in acetonitrile, the triazine (III) was isolated:[62,67,123]



(III)

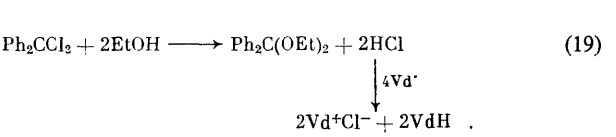
Compound (III) is apparently formed via an intermediate arylchlorocarbene or via the recyclisation of the verdazyl alkylation product.

Reaction (18) takes place[68] in the heterolysis of Ph_2CCl_2 in aprotic solvents in the presence of verdazyl and its rate is described by Eqn. (16):



The verdazyl alkylation product is apparently formed initially and then decomposes rapidly into $Vd^{+}Cl^{-}$ and diphenylcarbene. The latter is oxidised by oxygen to benzophenone.

The heterolysis of Ph_2CCl_2 takes place in ethanol in accordance with the equation:[69]



In conformity with the stoichiometry of this reaction, its rate in each individual experiment is described by a pseudo-zero-order kinetic equation:

$$-d[Vd^{\cdot}]/4dt = d[Vd^{+}Cl^{-}]/2dt = k_0. \quad (20)$$

In 85% aqueous dioxane, the verdazyl alkylation product Ph_2CCl_2 is stable during the kinetic experiment and the rate of reaction is described in this case by the kinetic equation (8).[69,77] Thus the stoichiometric ratios $[Ph_2CCl_2]:[Vd^{\cdot}]:[Ph^{+}Cl^{-}]$ depend greatly on the nature of the solvent in the heterolysis of the Ph_2CCl_2 in the presence of verdazyl. In an aprotic medium, they are 1:2:2, in ethanol they are 1:4:2, and in 85% aqueous dioxane they are 1:2:1.

A similar wide variety of stoichiometric ratios has been observed also in the heterolysis of trichloromethylbenzenes.[61,62,66,76] This is a characteristic feature of organic polychloro-compounds which afford unstable alkylation products on interaction with verdazyl.

A characteristic feature of the verdazyl method is that the indicator always reacts with the solvent-separated ion pair of the substrate. This occurs also in an aprotic medium where there is no

nucleophile other than Y—Vd· and in a protic medium where verdazyl must compete with a solvent molecule for the cationoid. For example, in 85% aqueous dioxane in the presence of 1×10^{-4} M Vd·, the heterolysis of Ph_2CCl_2 and p-$MeOC_6H_4CHCl_2$ takes place fully via the pathway leading the formation of verdazyl alkylation products and not hydrolysis products. This shows that the solvent-separated ion pair reacts very rapidly with verdazyl.

The verdazyl method made it possible to investigate in detail the influence of small amounts of water (0.05—0.3 M) on the rates of S_N1 and $E1$ reactions in aprotic solvents and to determine the relative yields of products formed with participation of Y—Vd· and water in S_N1 reactions.[18,21,39,41—44,46,47,49,50,52,54,59,62,69,70] Water cooperates with the heterolysis reactions in all cases by virtue of the formation of hydrogen-bonded complexes ($RX\ldots H_2O$) and increases the rate of reaction. The kinetic effect of water is determined by the parameter b in Winstein's equation (21) and greatly depends on the nature of the substrate and the solvent:

$$k_{H_2O}=k(1+b[H_2O]). \qquad (21)$$

Here k_{H_2O} and k are the rate constants for heterolysis in the presence of water and in its absence.

The kinetic effect of water yields information about possible errors in the determinatin of the rate of heterolysis due to undetermined admixtures of water in the aprotic solvent. The lowest value of b (1—3 litre mol^{-1}) were found for the heterolysis of t-butyl and adamantyl substrates. Usually b = 5—10 litre mol^{-1}, reaching 30—50 litre mol^{-1} in some cases (7α-bromocholesteryl benzoate in PhCN and $PhNO_2$).[59,70] Analysis of the data presented shows that the undetermined admixtures of water (<0.05 M) have hardly any effect on the rate of heterolysis of t-BuX and 1-AdX in aprotic solvents; for b = 10 litre mol^{-1}, the error in the determination of the rate can be 10—15%, while for b = 50 litre mol^{-1} the error is 30%. The values quoted refer to polar aprotic solvents (MeCN, propylene carbonate, $PhNO_2$, PhCN). On reducing the polarity of the solvent, the kinetic effect of water increases, but the water content then falls so much that the real effect becomes insignificant.

On heterolysis of Ph_2CHX (X = Cl, Br) in the presence of Vd· in moist acetonitrile with $[H_2O] \simeq 0.045$ M, two reaction products are formed from the substrate—the verdazyl alkaylation product and diphenylmethanol:[21,39]

$$Ph_2CHX \begin{cases} \xrightarrow{2Vd^{\cdot}} Ph_2CH{-}Vd + Vd^+X^-, \\ \xrightarrow{H_2O} Ph_2CHOH + HX \end{cases} \qquad (22)$$

$$HX \xrightarrow{2Vd^{\cdot}} Vd^+X^- + VdH\ .$$

Regardless of the relative yields of these products, the rate of reaction is described by the kinetic equation (8).

The method makes it possible to determine the amount of Ph_2Cd—Vd and VdH formed in the kinetic experiment. As already mentioned, an equimolecular mixture of Vd^+X^- and VdH is quantitatively converted into Vd· when acted upon by alkali. If formaldehyde is added, then the excess Vd^+X^- is also converted quantitatively into verdazyl.[124,125] In practice, this is achieved by adding a drop of an alkaline solution of formaldehyde to the reaction mixture. Since the relative yields of Ph_2Cl—Vd and VdH are determined by the competition between Vd· and H_2O for the formation of the solvent-separated ion pair $Ph_2CH^+|Solv|X^-$, then, knowing the concentrations of both nucleophiles in the solution, it is possible to calculate their relative reactivities in the reaction with the solvent-separated ion pair. In the heterolysis of Ph_2CHX (X = Cl, Br) in MeCN at 25 °C, the ratio $k_{Vd^{\cdot}}/k_{H_2O} \simeq 10^4$. Consequently Vd· is a very powerful nucleophile compared with H_2O. Indeed in the case of a strong nucleophile such as N_3^-, the ratio k_{N_3}/k_{H_2O} for Ph_2CHCl is only 170.[126]

In the heterolysis of 1-AdI in moist acetonitrile, $k_{Vd^{\cdot}}/k_{H_2O} \simeq 10^4$, while in the heterolysis of 1-AdOTs the ratio is $\sim 10^3$.[46,49]

The high reactivity of verdazyl compared with water in the reaction with the solvent-separated ion pair is apparently due to the different mechanisms of these reactions—the reaction with H_2O involves an S_N2 process during which the cationoid should be desolvated, while the reaction with Vd^+ apparently involves an outer-sphere electron transfer (an $SET2$ reaction) without the decomposition of the solvation shells of the reactants. This explains why triphenylverdazyls proved to be such effective internal indicators for unimolecular heterolysis reactions.

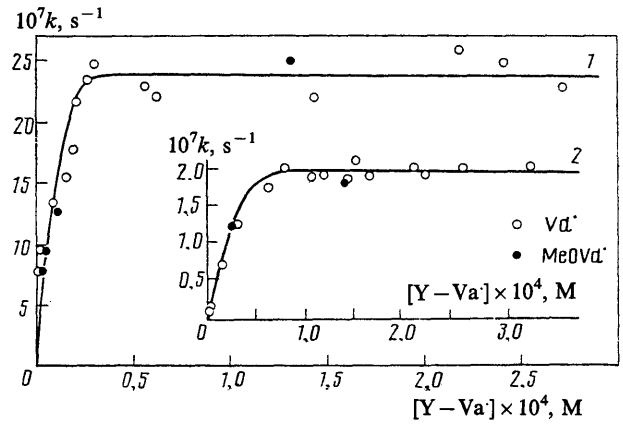


Figure 3. The influence of the concentration and nature of Y—Vd· on the rate of heterolysis of Ph_2CCl_2 in acetonitrile (line *1*) and acetone (line *2*) at 25 °C.

The data currently available for the heterolysis of organic substrates in the presence of verdazyls (Ph_2CHBr,[40—45,72] Ph_2CHCl,[21] 1-AdOTs,[46,54,56,80] 1-AdI,[47,49] 1-AdOCOCl,[27] 1-AdOPic,[52,56,80] 7α-bromocholesteryl benzoate,[59,70,75] PhCHClMe,[60,65,69] p-MeO.$C_6H_4CCl_3$,[62] Ph_2CCl_2,[69,77] t-BuBr,[68,73] t-BuCl,[71] p-$MeOC_6H_4$.$CHCl_2$,[77,78] cumenyl chloride,[79] 2-bromo-2-methyladamantane,[68] and 2-chloro-2-methyladamantane[71]) show that these radicals always react with the solvent-separated ion pairs of the substrate—both in S_N1, $E1$, and $F1$ reactions and in solvolytic reactions. This is a characteristic feature of the verdazyl method. The solvent-separated ion pair is formed after the rate-limiting stage of the heterolysis. Clearly verdazyls can be used as indicators subject only to the condition that the rate of the reaction of the solvent-separated ion pair with Y—Vd· is higher than the rate of formation of this intermediate. It is easy to assume that, on reducing the

concentration of the indicator, it is possible to achieve a situation where the reaction of Y—Vd˙ with the solvent-separated ion pair limits the overall rate of the process. This has been demonstrated in the heterolysis of Ph_2CCl_2,[69,77] p-$MeOC_6H_4CHCl_2$,[77,78] and $(p\text{-}ClC_6H_4)_2CCl_2$.[69]

The influence of the concentration and nature of the verdazyl on the rate of heterolysis Ph_2CCl_2 in acetonitrile and acetone is illustrated in Fig. 3, while Fig. 4 demonstrates their influence on the rate of solvolysis of Ph_2CCl_2 and p-$MeOC_6H_4CHCl_2$ in 85% aqueous dioxane.

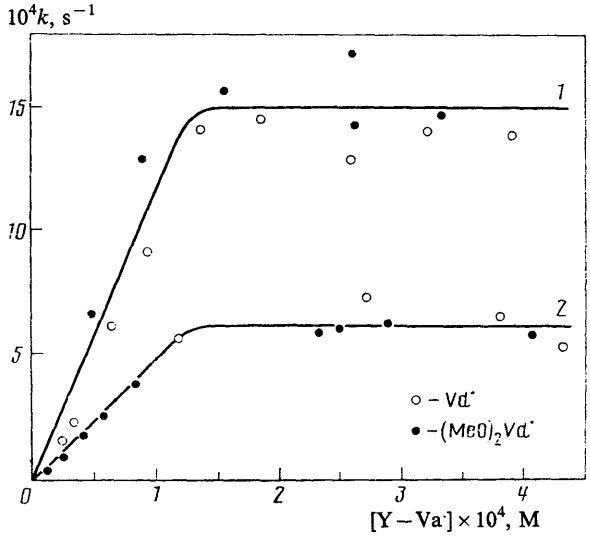


Figure 4. The influence of the Vd˙ concentration on the rate of heterolysis of p-$MeOC_6H_4CHCl_2$ (line *1*) and Ph_2CCl_2 (line *2*) in 85% aqueous dioxane.

Evidently the k—[Y—Vd˙] relation consists of two sections; at relatively high indicator concentrations, the rate of reaction is independent of the concentration of Y—Vd˙ and of the nature of its substituent, while at low indicator concentrations a direct proportionality is observed between the quantity k and the Y—Vd˙ concentration. In the former case, the rate of reaction is described by Eqn. (4), while in the latter it is described by a second-order kinetic equation:

$$v = k_2[RX][Y—Vd˙]. \quad (23)$$

Thus, on reducing the indicator concentration, the rate-limiting state of the reaction changes: at comparatively high verdazyl concentrations, the rate-limiting stage involves the formation of a cationoid intermediate (S_N1 reaction), while at a low verdazyl concentration Y—Vd˙ reacts with the solvent-separated ion pair of the substrate (*SET*2 reaction) in the rate-limiting stage.

The change in the kinetic relations and hence the change in the reaction mechanism in the heterolysis of Ph_2CCl_2 in acetonitrile, acetone (Fig. 3), ethanol (not shown in the Figure), and 85% aqueous dioxane (Fig. 4) occurs at Vd^+ concentrations of 2.0×10^{-5}, 6.2×10^{-5}, 11×10^{-5}, and 13×10^{-5} M respectively. In γ-butyrolactone and propylene carbonate, the rate of reaction is independent of the indicator concentration up to [Vd˙] ≃ 2×10^{-6} M. In the solvolysis of p-$MeOC_6H_4CHCl_2$ in 85% aqueous dioxane, the kinetic relations change at a verdazyl concentration of 11×10^{-5} M (Fig. 4). In the solvolysis of $(p\text{-}ClC_6H_4)_2CCl_2$ in alcohols, the change occurs at [Vd˙] > 1×10^{-4} M.[69] These data demonstrate that, when verdazyls are used in a proton-donating medium, the indicator concentration must be higher than 1×10^{-4} M, whereas in an aprotic medium it can be appreciably lower. In the study of the kinetics of the heterolysis of organic compounds by the verdazyl method, it is necessary to obtain proof that the rate of reaction is independent of the indicator concentration for each reaction system.

It is seen from Figs. 3 and 4 that the rates of heterolysis of Ph_2CCl_2 and p-$MeOC_6H_4CHCl_2$ are independent of the nature of the substituent in the verdazyl even when the rate of reaction depends on its concentration. This demonstrates that the reaction of Y—Vd˙ with the solvent-separated ion pair consists of many stages: in one stage, verdazyl plays the role of an electron donor (formation of a charge-transfer complex), whilst in another it behaves as an electron acceptor (decomposition of the charge-transfer complex), which leads to the compensation effect of the substituent in the indicator. Thus, by changing the concentration of the indicator, it is possible to change the rate-limiting stage of the reaction and to obtain information about the mechanism of the product-forming stage.

In the course of the development of the verdazyl method, important conclusions were reached concerning the essential features of the unimolecular heterolysis of organic compounds investigated. The application of the method demonstrated that the stage involving the external return of the ion pair ($R^+|Solv|X^- \rightarrow R^+X^- \rightarrow RX$) is not very important, although this idea is still always used in the interpretation of the reaction mechanism.[7—9,40,45,109,110] If this stage could influence appreciably the overall rate of reaction, the rate constant determined in the presence of verdazyl would have depended on the concentration and nature of Y—Vd˙ owing to the competitive decompositon of the solvent-separated ion pair in the ion pair recovery reaction and the reaction with the indicator:

$$RX \leftarrow R^+X^- \leftarrow R^+|Solv|X^- \xrightarrow{Vd˙} \text{products}.$$

Hitherto this has never been observed in the study of the kinetics of the heterolysis of all the substrates listed above in various protic and aprotic solvents.

Since the data obtained by the verdazyl method agree well with the results of other procedures, one may claim that the stage involving the external return of the ion pair is not very important both in the presence of verdazyls and without them, although the opposite view is frequently adhered to in the literature.[7,109,110,113,116,117] For example, it is believed[116,117] that the rates of solvolysis of Ph_2CCl_2 and p-$MeOC_6H_4CHCl_2$ in 85% aqueous dioxane, determined spectrophotometrically from the formation of Ph_2CO and p-$MeOC_6H_4CHO$, depend greatly on the stage involving the external return of the ion pair and it is postulated that the rate-limiting stage involves the interaction of the solvent-separated ion pair of the substrate with water. It has been demonstrated by the verdazyl method[69,77,78] that, under conditions where the rate of reaction is independent of the concentration and nature of Y—Vd˙, the results of both studies agree satisfactorily. Consequently in both cases the mechanism of the external return of

the solvent-separated ion pair is unimportant. Under the conditions of the studies of Vitullo and Vilgis,[116,117] the solvent-separated ion pair reacts with water, while under the conditions of the studies of Dvorko and co-workers[69,77,78] it reacts with Y—Vd˙. The agreement between the rate constants shows that the rate-limiting stage in these reactions is the formation of the cationoid intermediate and not the reaction of the solvent-separated ion pair with the nucleophile.

The application of the verdazyl method makes it possible to shorten greatly the time required to study the kinetics of the heterolysis reactions and to obtain reliable data in those cases where the rate of reaction depends comparatively greatly on the salt concentration. This made it possible to determine the rates of heterolysis of the majority of the substrates listed above in a large set of protic and aprotic solvents (20—40 solvents) and to carry out a quantitative analysis of the solvation effects.[11,34,48,51,53,55—57,64—66,68—70,76] It was shown that the rate of reaction is determined mainly by the polarity and electrophilicity of the solvent and that the nucleophilic cooperation of the solvent with the heterolysis does not take place. The rates of heterolysis of PhCHClMe, Ph_2CHBr, 1-AdOTs, and $PhCMe_2Cl$ are altogether independent of the nucleophilic properties of the medium, while in the heterolysis of 7α-bromocholesteryl benzoate, t-butyl halides, 1-AdI, 1-AdBr, 1-AdOPic, 2-bromo-2-methyladamantane, and p-$MeOC_6H_4CCl_3$, the negative effect of nucleophilic solvation is observed.

If the rate of heterolysis has been limited by the conversion of the contact ion pair into the solvent-separated ion pair (Scheme 3), as is generally assumed,[7,8,10] the nucleophilicity of the solvent would have promoted the reaction. In order to overcome this contradiction, a new intermediate was introduced into Winstein's scheme—a space-separated ion pair (SPSIP), formed on conversion of the contact ion pair into the solvent-separated ion pair:[49,60,62,68—70]

$$RX \rightleftharpoons R^+X^- \rightleftharpoons \underset{\text{SPSIP}}{R^+ \ldots X^-} \rightleftharpoons R^+|Solv|X^-. \qquad (24)$$

It is postulated that the rate-limiting stage of the heterolysis is the separation of ions in the contact ion pair with formation of a vacancy between them. Consequently a solvent molecule is rapidly incorporated in the interionic space within the space-separated ion pair.

On solvolysis of organic substrates via the S_N2—ion pair mechanism ($PhCH_2Cl$, PhCOCl, allyl tosylate), the rate of reaction increases with increasing nucleophilicity of the solvent.[37,61]

The application of the verdazyl method to the study of an *F*1 reaction for 1-AdOCOCl as an example yielded an unexpected resut:[27,56] the rate constants [Eqn. (4)] found in protic and aprotic solvents differed as a rule from the values obtained from the consumption of the substrate.[26,127] This is associated with the fact that the decomposiiton reaction of 1-AdOCOCl is a consecutive-parallel process and different methods for the determination of the reaction rate reflect different aspects of this process. The data obtained supplement one another. This leads to new possibilities for the study of *F*1 reactions. The use of verdazyls made it possible to demonstrate the fragmentation process proceeds via the formation of both a contact ion pair and a solvent-separated ion pair.

The rate of heterolysis of organic substrates is determined under the conditions of a stationary process where the concentration of cationoid intermediates [Int] remains constant during the kinetic experiment, i.e. for $d[Int]/dt = 0$.[128] However, time is required for the reaction system to attain a stationary state. The verdazyl method makes it possible in some cases to follow the process by determining the rate at very low conversions of the substrate ($\sim 10^{-4}$—10^{-5}%). This was observed in the heterolysis of Ph_2CCl_2 in propylene carbonate[69] and of cumenyl chloride in acetonitrile, propylene carbonate, and γ-butyrolactone.[79] In these cases, and induction period, reflecting the attainment of the stationary state by the system, appears (Fig. 5) on the kinetic curve. A delay in the attainment of a stationary state by the system may be caused by undetermined impurities in the solvent and by added salts (LiBr, $Bu_4N^+Br^-$, $Et_3PhCH_2N^+Cl^-$) or a crown-ether. These compounds apparently trap the intermediate formed before the rate-limiting stage (for example, a contact ion pair) and for a time direct the process towards the formation of an inactive complex. The addition of $LiClO_4$, which catalyses the conversion of the contact ion pair into an intermediate with a greater degree of charge separation, eliminated the induction period.

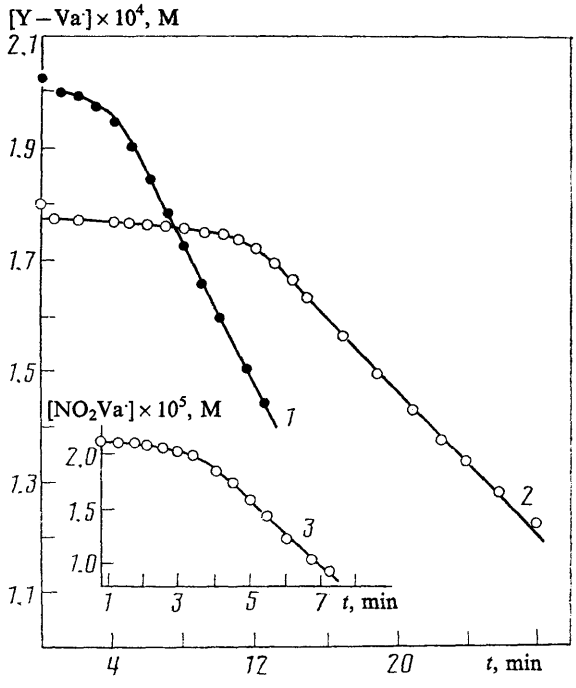


Figure 5. Kinetics of the heterolysis of $PhCMe_2Cl$ in propylene carbonate in the presence of salts at 25 °C: *1*, $[PhCMe_2Cl] = 0.00645$ M, $[Vd˙] = 2.03 \times 10^{-4}$ M, $[Bu_4N^+Br^-] = 0.1$ M, $k = 8.03 \times 10^{-6}$ s^{-1}; *2*, $[PhCMe_2Cl] = 0.00688$ M, $[(MeO)_2Vd˙] = 1.80 \times 10^{-4}$ M, $[Et_3(PhCH_2)N^+Cl^-] = 0.05$ M, $k = 4.30 \times 10^{-6}$ s^{-1}; *3*, $[PhCMe_2Cl] = 0.00636$ M, $[NO_2Vd˙] = 2.2 \times 10^{-5}$ M, $[LiBr] = 0.0599$ M, $k = 4.02 \times 10^{-6}$ s^{-1}.

III. Application of the verdazyl method to the study of salt effects

Salt effects constitute a fine instrument for the investigation of the details of the mechanisms of organic reactions and for the establishment of the nature of the catalytic effects.[1,7,8] This is one of

the most difficult problems in physical organic chemistry. The application of verdazyls makes it possible to study in detail the salt effects in heterolysis reactions, to elucidate their nature, and to specify in a concrete form the mechanism of the heterolysis itself. Particularly valuable data have been obtained in the study of S_N1 and $E1$ reactions in an aprotic medium.[40,43,45–47,49,50,52,54,56,61,62,65,68–73,75,76–80]

The interpretation of the unusual salt effect of perchlorate put forward by Winstein has given rise to much controversy.[1,7–9,40,45,129] It reduces to the postulate that the sharp increase in the rate of reaction in the presence of small amounts of the salt is caused by the exchange of the nucleofugal species in the solvent-separated ion pair with formation of the ion pair (IV), which is incapable of being converted into a contact ion pair:

$$\underset{}{ClO_4^-}+R^+|Solv|X^- \rightleftharpoons \underset{(IV)}{R^+|Solv|ClO_4^-}+X^- \quad . \qquad (25)$$

In other words, the presence of the unusual salt effect is explained by the suppression of the stage involving the external return of the ion pair. As already mentioned, it has been demonstrated with the aid of the verdazyl method that this stage is unimportant. Winstein's intepretation is incorrect.[40,43,45] Detailed study of the unusual salt effect by the verdazyl method led to the conclusion that the catalytic effect of perchlorate is caused by the effect of ClO_4^-,[40] Li^+,[70,75] or of the salt ion pair[68–70] on the contact ion pair of the substrate, which leads to the formation of the ion triplets (V) and (VI) or the quadrupole (VII), which are converted more readily than the contact ion pair itself into the cationoid intermediate with a greater charge separation:

$$\underset{(V)}{ClO_4^-|Solv|R^+X^-}, \quad \underset{(VI)}{R^+X^-Li^+}, \quad \underset{(VII)}{R^+X^-, M^+Y^-} \quad .$$

Comparison of data for the kinetics of the hydrolysis of Ph_2CCl_2 in acetone, obtained by the verdazyl method,[69] with the results of a study[130] where the reaction of Ph_2CCl_2 with NaI was investigated in the same solvent in the presence of $LiClO_4$ provided evidence in support of the fact that the catalytic effect of $LiClO_4$ under the conditions of the unusual salt effect is caused by the action of the salt on the contact ion pair and not on the covalent substrate. In the latter case, the catalytic effect of the salt is lower by approximately two orders of magnitude.

Analysis of data for other positive salt effects, obtained by the verdazyl method, showed that they are associated with the formation of the quadrupole (VII) and not with the increase in the ionic strength of the solution.[21,40,43,46,47,49,52,54,62,68–71] The unusual salt effect is a variety of the normal salt effect.

The concentration and nature of Y—Vd$^{\cdot}$, both in the presence of salts increasing the rate of reaction and in their absence, do not affect the rate of reaction.

The verdazyl method has also made it possible to discover a new salt effect, which was called the negative salt effect.[40,43,46,47,49,52,54,56,62,68–71,76,80] Its characteristic feature is that of the addition of a salt having an ion in common with the ion pair lowers the rate of reaction under conditions where a free carbonium ion is not formed. Such reduction in the rate of reaction is usually attributed to the salt effect caused by the Law of Mass Action, i.e. by the reaction involving reformation from the free carbonium ion:[1–3,7–9,129]

$$R^+ + X^- \rightarrow R^+|Solv|X^- \rightarrow R^+X^- \rightarrow RX.$$

However, the negative salt effect is usually manifested in an aprotic medium where heterolysis does not go so far as the formation of a free carbonium ion.

This salt effect is associated with the reaction involving the external return of the ion pair: the salt or its anion form with the solvent-separated ion pair or the space-separated ion pair a quadrupole or an anionic triplet, which are more readily converted into the contact ion pair and subsequently into the covalent substrate than the solvent-separated and space-separated ion pairs themselves:

$$RX \rightleftharpoons R^+X^- \overset{X^-}{\rightleftharpoons} R^+ \ldots X^- \rightleftharpoons R^+|Solv|X^- \xrightarrow{Y-Vd^{\cdot}} \text{products}. \qquad (26)$$

The decrease in the rate of reaction in the presence of a salt with a common ion is caused by the catalysis of the reaction involving the external return of the ion pair.

For low degrees of conversion of the substrate, where the nucleofugal species exchange reaction is unimportant, a negative salt effect of a similar kind is manifested also in the presence of a salt with a non-common ion. In all cases its nature is the same: a decrease in the concentration of the product-forming intermediate (a solvent-separated ion pair).

It is seen from Scheme (26) that the verdazyl always acts on the solvent-separated ion pair, while the salt can act both on the solvent-separated ion pair and on the space-separated ion pair. In the former case, there is competition between the salt and the verdazyl for the cationoid and the rate of reaction should depend on the nature and concentration of Y—Vd$^{\cdot}$. In the latter case, this should not be observed.

Detailed study of the influence of the concentration of the verdazyl and of the nature of the substituent in it on the rate of reaction in the presence of salts reducing the rate of reaction demonstrated that the nature of the negative salt effect depends greatly on the structure of the substrate and on the nature of the salt and the solvent. Thus the decrease in the rate of heterolysis of *p*-$MeOC_6H_4CCl_3$ in acetonitrile in the presence of LiCl is caused by the interaction of the salt with the space-separated ion pair.[62] A similar picture is observed in the heterolysis of 1-AdI in propylene carbonate in the presence of $Et_4N^+OPiC^-$.[49] In the heterolysis of Ph_2CCl_2 in acetonitrile, γ-butyrolactone, and propylene carbonate, the negative salt effect of chlorides and bromides is associated with their interaction with the solvent-separated ion pair,[69] whereas in the heterolysis of 7α-bromocholesteryl benzoate in γ-butyrolactone, the negative salt effect of the chloride is caused by the reaction of the salt with the space-separated ion pair while in nitrobenzene and *o*-xylene it is due to interaction with the solvent-separated ion pair.[70] The negative salt effect of $Et_3(PhCH_2)N^+Cl^-$ in the heterolysis of cumenyl chloride in acetonitrile and γ-butyrolacetone is also associated with the effect of the salt on the solvent-separated ion pair, while propylene carbonate it is due to its effect on the space-separated ion pair, while in propylene carbonate it is due to its effect on the space-separated ion pair.[79] In the heterolysis of t-BuBr, t-BuCl, 2-bromo-2-methyladamantane, and 2-chloro-2-methyladamantane, and 2-chloro-methyladamantane in γ-butyrolactone, the negative salt effect of the chloride and thiocyanate is associated with their interaction with the solvent-separated ion pair.[68,73] On the other hand, in the heterolysis of Ph_2CHBr in acetonitrile the salts $Et_4N^+I^-$ and $Et_4N^+Br^-$ act on the space-separated ion pair, while

$Et_4N^+Cl^-$ and $Et_3(PhCH_2)N^+Cl^-$ act on the solvent-separated ion pair.[40,72]

When the rate of heterolysis in the presence of a salt reducing the rate of reaction depends on the Y—Vd˙ concentration, then it usually depends also on the nature of the substituent in the indicator, the rate increasing with enhancement of the electron-donating properties of the radical. This is associated with the idea that the reaction of the solvent-separated ion pair with Y—Vd˙ proceeds via electron transfer from the radical to the cationoid.[91–96] In the heterolysis of Ph_2CCl_2 in acetonitrile in the presence of chlorides, the rate of reaction increases with increasing Y—Vd˙ concentration but is independent of the nature of the substituent in the radical,[69] while in the heterolysis of Ph_2CHBr in acetonitrile in the presence of $Et_3(PhCH_2)N^+Cl^-$ the rate of reaction falls on enhancement of electron-donating properties of Y—Vd˙.[72] These data confirm the conclusion that the reaction between the solvent-separated ion pair and Y—Vd˙ proceeds in several stages.

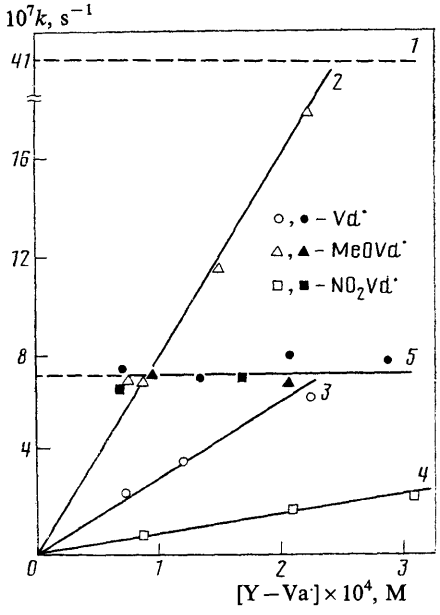


Figure 6. The influence of the concentration and nature of Y—Vd˙ on the rate of heterolysis of 1=AdOTs in γ-butyrolactone in the presence of 0.03 M $Et_4N^+Cl^-$ (lines *2–4*) and 0.03 M $Et_4N^+Br^-$ (line *5*) at 35 °C and in the absence of salts (line *1*).

The study of the k—[Y—Vd˙] relations in the presence of salts reducing the rate of reaction makes it possible to observe also fine differences between salt and solvation effects. Thus the rate of heterolysis of 1-AdOTs and 1-AdOPic in acetonitrile, γ-butyrolactone, and propylene carbonate in the presence of $Et_3(PhCH_2)N^+Cl^-$ or $Et_4N^+Cl^-$ increases with increase in the concentration of Y—Vd˙ and with increase in its electron-donating properties[52,54,56] (Figs. 6–9). Consequently the negative salt effect of the chloride is caused by the reaction of the salt with the solvent-separated ion pair. The addition of $Et_3N^+Br^-$ in the heterolysis of the substrates indicated in γ-butyrolactone and propylene carbonate also reduces the rate of reaction but only in the case of 1-AdOPic in γ-butyrolactone (Fig. 7) does the rate of reaction in the presence of this salt depend on the concentration and nature of Y—Vd˙. Consequently the verdazyl and the chloride act in all these cases on the solvent-separated ion pair, whereas the bromide ion acts on the solvent-separated ion pair in some instances and on the space-separated ion pair in others. On the other hand, in acetonitrile, where the positive salt effect o $Et_4N^+Br^-$ is manifested, the latter salt acts on the contact ion pair.

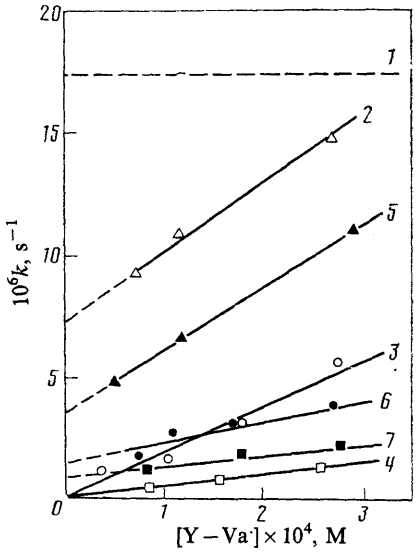


Figure 7. The influence of the concentration and nature of Y—Vd˙ on the rate of heterolysis of 1-AdOPic in γ-butyrolactone in the presence of 0.03 M $Et_3(PhCH_2)N^+Cl^-$ (lines *2–4*) and 0.03 M $Et_4N^+Br^-$ (lines *5–7*) at 25 °C [*1*, the heterolysis rate constant in the absence of salts]; verdazyl: *2* and *5*, $(MeO)_2$Vd˙; *3* and *6*, Vd˙; *4* and *7*, NO_2Vd˙.

Analysis of the nature of the salt effects in an aprotic medium[80] has shown that ClO_4^- acts on the contact ion pair, Br^- acts as a rule on the space-separated ion pair, while Cl^- acts on the solvent-separated ion pair, i.e. with increase in the hardness of the anion there is an increase in the tendency of the salt to react with the later intermediate—with the cationoid having a greater charge separation. Consequently the site where the salt acts during the ionisation of the covalent bond is determined by the principle of hard and soft acids and bases (HSAB), because an increase in the hardness of the carbonium ion is to be expected in the CIP—SPSIP—SSIP series.

The differences between the space-separated and solvent-separated ion pairs are apparently small and their negative activity in the reaction with the salt therefore depends greatly both on the structure of the substrate and on the nature of the solvent.[52,56,70–72,77–79] In the solvolysis of *p*-$MeOC_6H_4CHCl_2$ in aqueous dioxane, Cl^- acts on the space-separated ion pair, while Br^- acts on the solvent-separated ion pair,[78] which is caused by the inversion of the

nucleophilicity of the halide anion in water compared with the aprotic medium.

The application of the HSAB principle to the interpretation of the salt effects in unimolecular heterolysis reactions and other carbonium ion processes[131,132] makes it possible to explain why the catalytic effect in the carbonium generation process is manifested by the weakest nucleophile. This is associated with the fact that it begins to act in the earliest stages.

The application of the verdazyl method showed that, in the heterolysis of organic substrates, a superposition of the positive and negative salt effects is frequently observed.[52,54,56,65,68–71,73]

Figs. 8 and 9, where the $k-[Y-Vd^{\cdot}]$ relations are presented for the heterolysis of adamantyl substrates in acetonitrile in the presence of chlorides, show that the form of the $k-[Y-Vd^{\cdot}]$ curves for 1-AdOTs differs significantly from that for 1-AdOPic. In the case of 1-AdOTs (Fig. 8), an increase in the $Y-Vd^{\cdot}$ concentration results in the attainment of by k of the value of the rate constant for heterolysis in the absence of salts (indicated by a dashed line), after which k no longer changes on increase in the indicator concentration. In the heterolysis of 1-AdOPic, the value of the rate constant for heterolysis in the absence of salts is also rapidly attained as the indicator concentration rises, but in this case k continues to increase on further increase in the indicator concentration. This shows that in the latter case the negative salt effect is accompanied also by a positive salt effect, which is due to the action of the salt on the contact ion pair.

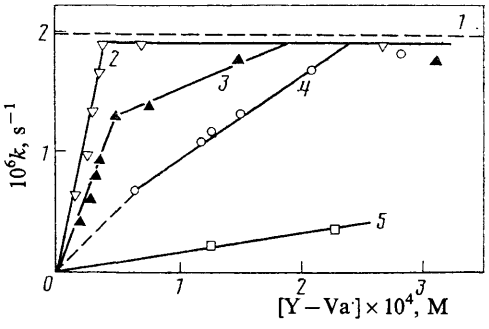


Figure 8. The influence of the concentration and nature of $Y-Vd^{\cdot}$ on the rate of heterolysis of 1-AdOTs in acetonitrile in the presence of 0.03 M $Et_4N^+Cl^-$ at 25 °C [*1*, the heterolysis rate constant in the absence of salts]; verdazyl: *2*, $(MeO)_2Vd^{\cdot}$; *3*, $MeOVd^{\cdot}$; *4*, $Vd^{\cdot}$; *5*, $NO_2Vd^{\cdot}$.

The superposition of the salt effects is manifested particularly well when one follows the influence of the salt concentration on the rate of reaction in the presence of the same concentration of verdazyls. Fig. 10 shows how markedly the manifestation of the salt effect changes as a function of the nature of the indicator in the heterolysis of t-BuBr in γ-butyrolactone in the presence of $Et_3(PhCH_2)N^+Cl^-$:[68,73] in the presence of $MeOVd^{\cdot}$, the salt hardly affects the rate of reaction, in the presence of $Vd^{\cdot}$ and $NO_2Vd^{\cdot}$ the rate of reaction falls with increase in the salt concentration, while in the presence of $(MeO)_2Vd^{\cdot}$ it increases. These relations can be explained by the superposition of the negative and positive effects of $Et_3(PhCH_2)N^+Cl^-$, the negative salt effect being due to the reaction in the salt (as well as the verdazyl) with the solvent-separated ion pair, while the positive effect is due to the reaction with the contact ion pair. In the presence of $MeOVd^{\cdot}$, both effects are approximately the same, in the presence of $Vd^{\cdot}$ and especially $NO_2Vd^{\cdot}$ the negative salt effect predominates, while in the presence of $(MeO)_2Vd^{\cdot}$, which traps the solvent-separated ion pair almost completely and hence suppresses the negative salt effect, the positive salt effect predominates.

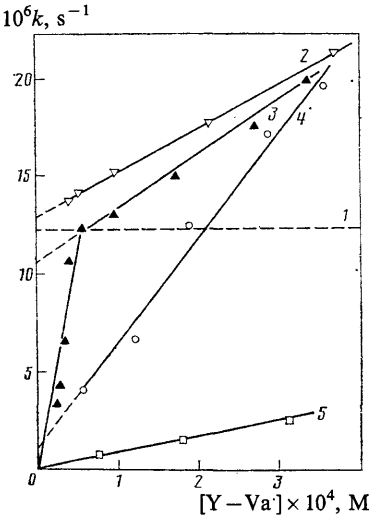


Figure 9. The influence of the concentration and nature of $Y-Vd^{\cdot}$ on the rate of heterolysis of 1-AdOTPic in acetonitrile in the presence of 0.03 M $Et_3(PhCH_2)N^+Cl^-$ at 25 °C [*1*, the heterolysis rate constant in the absence of salts]; verdazyl: *2*, $(MeO)_2Vd^{\cdot}$; *3*, $MeOVd^{\cdot}$; *4*, $Vd^{\cdot}$; *5*, $NO_2Vd^{\cdot}$.

It is seen from Figs. 8–10 that at certain $Y-Vd^{\cdot}$ concentrations the negative salt effect is completely eliminated. The relative reactivities of the verdazyl and the salt in the reaction with the solvent-separated ion pair were calculated from these data.[52,54,56,69,70–79] In the heterolysis of 1-AdOTs, 1-AdOPic, $PhCMe_2Cl$, and t-BuBr, the solvent-separated ion pair reacts ~2 orders of magnitude faster with the verdazyl than with the salt. This agrees with the hypothesis that $Y-Vd^{\cdot}$ reacts with the solvent-separated ion pair and not with the free carbonium ion. In the heterolysis of Ph_2CCl_2, the verdazyl and the chloride react with the sovent-separated ion pair at approximately the same rates.[69]

The decrease in the rate of heterolysis in the presence of a salt having a common ion is almost always explained by the salt effect caused by the Law of Mass Action, i.e. by the formation of a free carbonium ion [see Scheme (3)].[1,3,8,129] It was demonstrated above that such a decrease in the rate can be associated with the action of the salt on the solvent-separated or space-separated ion pair. The verdazyl method makes it possible to specify in a more concrete form the cause of the decrease in the rate of reaction in the presence of a salt having a common ion.

As an example, we shall consider the heterolysis of p-$MeOC_6H_4CHCl_2$. The rate of solvolysis of this substrate has been determined[117] in 75% aqueous dioxane from the formation of p-$MeOC_6H_4CHO$. It was shown that the addition of chlorides (LiCl, $Bu_4N^+Cl^-$) diminishes the rate of reaction; it was concluded that the reaction proceeds via the formation of a fre carbonium ion. The study of the kinetics of the solvolysis of p-$MeOC_6H_4CHCl_2$ by the verdazyl method under similar conditions showed that Cl^- and the verdazyl act on different intermediates.[78] If it is supposed that Vd$^\cdot$ reacts with the free carbonium ion, then Cl^- should react with the solvent-separated ion pair. On the other hand if Vd$^\cdot$ reacts with the solvent-separated ion pair, then Cl^- should react with the space-separated ion pair. Consequently, in the heterolysis of p-$MeOC_6H_4CHCl_2$ in 75% aqueous dioxane, Cl^- never reacts with the free carbonium ions; the observed decrease in the rate of reaction is caused by the negative salt effect associated with the reaction of the salt with the substrate ion pair. In the solvolysis of p-$MeOC_6H_4CHCl_2$, a free carbonium ion is not formed.[78]

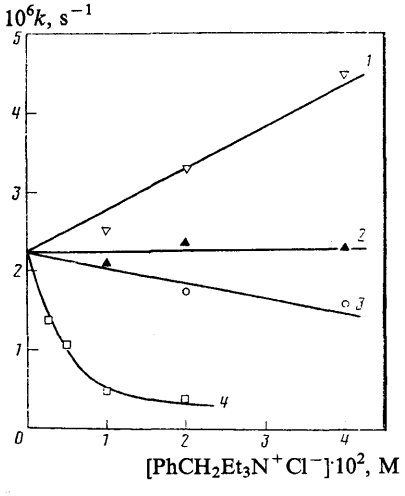


Figure 10. The influence of the concentration of $Et_3(PhCH_2)N^+Cl^-$ and of the nature of Y—Vd$^\cdot$ (3.2×10^{-4} M) on the rate of heterolysis of t-BuBr in γ-butyrolactone at 25 °C; verdazyl: *1*, $(MeO)_2Vd^\cdot$; *2*, $MeOVd^\cdot$; *3*, $Vd^\cdot$; *4*, $NO_2Vd^\cdot$.

The study by the verdazyl method of the salt effects in unimolecular heterolysis reactions confirmed the reaction mechanism represented by Scheme (24).

IV. Conclusion

The application of the verdazyl method to the study of the kinetics and mechanisms of S_N1, $E1$, and $N1$, and solvolysis reactions made it possible to reduce greatly the duration of the experiment and to obtain an extensive set of kinetic data which in many cases are inaccessible by other methods. These data have been used for the quantitative analysis of the solvation effects over a wide range of substrates. The application of the method to the study of S_N1 reactions has been shown to be especially effective. Other available methods for the study of the kinetics of these reactions generally yielded invalid results owing to the impossibility of taking into account the salt effects.

The application of the verdazyl method made it possible to investigate in detail the salt effects, to elucidate their nature, and to specify in detail the mechanism of the heterolysis of the covalent bond. For example, it has been shown that the conclusion that a free carbonium ion is formed, reached on the basis of the decrease in the rate of reaction in the presence of a salt with a common ion, is unjustified. In the study of $F1$ reactions, the verdazyl method proved to be an important complement to other procedures.

The verdazyl method has been widely tested.[18,21,22,27,29–80] The kinetics and mechanisms of the heterolysis of 21 substrates have been investigated with its aid. The results obtained for the solvation and salt effects have led to a new mechanism of the heterolysis of the covalent bond [see Scheme (24)] which includes the formation of a space-separated ion pair. It has been shown that the nature of the cationoid, which is subjected to nucleophilic attach by the salt anion, is determined by the principle of hard and soft acids and bases.

The verdazyl method is being vigorously developed at the present time. Further expansion and deepening of its possiblities should lead to significant mechanistic results.

The verdazyl method makes it possible to study the kinetics of the solvolysis of substrates, for example PhCOCl, which react via an S_N2 mechanism.[61] Verdazyls can also be used to study the kinetics of the photolysis of chlorohydrocarbons,[133,134] and for the selection of stabilisers for the latter.[135]

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