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Kinetics and Product Distribution of 1-Adamantyl Picrate Heterolysis in Acetonitrile in the Presence of Triphenylverdazyls

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Abstract—The reaction of triphenylverdazyls with strong acids in acetonitrile in the presence of salts with chloride anion is reversible. The observed rate of the heterolysis of 1-adamantyl picrate in the presence of triphenylverdazyls does not depend on the substituent in the latter and its concentration. The contribution of the verdazyl alkylation pathway is minor, the indicator is consumed mainly in the reaction with the acid liberated from the solvolysis. Thus, triphenylverdazyls are not indicators for the solvent-separated ion pairs.

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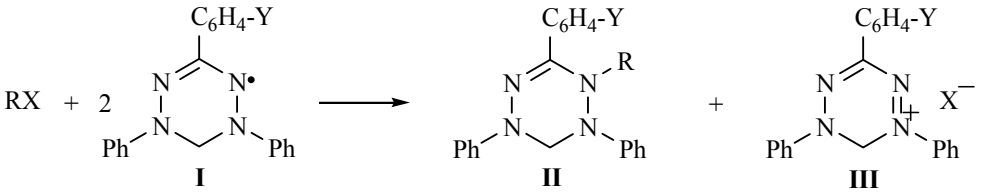
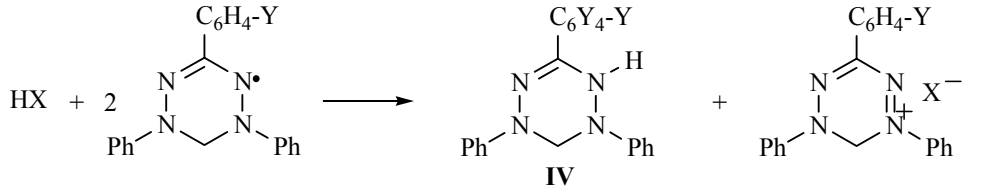
In their papers Dvorko and co-workers proposed and subtantiated the hypothesis [1, 2] that triphenylverdazyls (**I**) react in aprotic solvents selectively and quantitatively with the solvent-separated ion pairs formed during monomolecular heterolysis of the substrates [Eq. (1)].



(1)



(2)

On the contrary, our data [3, 4] on the product distribution of benzhydryl bromide heterolysis in acetonitrile, nitrobenzene and propylene carbonate, as well in acetonitrile in the presence of triethylbenzylammonium chloride, show that under these conditions triphenylverdazyl reacts predominantly with the acid released in the course of the solvolysis of the substrate [Eq. (2)]. It remained unclear, however, why in some cases [5–7] the observed reaction rate depended on the indicator structure and concentration. For example, in the heterolysis of 1-adamantyl tosylate and picrate in acetonitrile and propylene carbonate in the presence of triethylbenzylammonium chloride [8] a linear increase in the reaction rate with increasing the indicator concentration was observed, the radicals bearing electron-donating substituents being more reactive.

Such a dependence is formally indicative of the participation of triphenylverdazyls in the rate limiting or a competing product determining step. Obviously the reaction (2) cannot be one of these. Thus, it was necessary to find an alternative explanation for the observed kinetic and structural effects, if they are not associated with the verdazyl alkylation in the reaction (1).

Table 1. Dependence of the rate constant and contribution of the alkylation pathway in the reaction of heterolysis of 1-adamantyl picrate in acetonitrile at 25°C in the presence of triphenylverdazyl on the water content in the solvent

Exp. no.	c_{init}	c_0	c_{min}	c_{max}	α, %	$k\times10^6$, s^{-1}
	10^4 M					
1[a]	2.69	2.32	0.649	2.55	17	9.62±0.09
2[b]	2.37	2.00	0.831	2.28	16	5.14±0.05
3[c]	2.36	1.91	0.670	2.32	6	14.1±0.02

[a] Acetonitrile distilled over P_2O_5 and then over K_2CO_3. [b] Acetonitrile "Spectroscan," water content no higher than 6×10^{-4} M. [c] Acetonitrile "Spectroscan" with addition of water to 4.5×10^{-2} M.

The object of the present study was chosen for several reasons. First, only with 1-adamantyl and benzhydryl substrates Dvorko and co-workers obtained the products of verdazyl alkylation in their preparative experiments and studied the product distribution of the heterolysis reactions under kinetic conditions [1, 9]. Second, the kinetic and structural effects in this reaction in the presence of triethylbenzylammonium chloride are pronounced [8] and clearly exceed the possible error limits. Third, 1-adamantyl picrate is a highly reactive substrate and at the same time this compound is enough stable and easy to handle, in contrast to, for example, 1-adamantyl tosylate. Fourth, high purity acetonitrile is commercially available, allowing to maximally exclude the side reactions and to obtain the most reliable results.

Effect of water content in the solvent on the rate of heterolysis of 1-adamantyl picrate in the absence of salts. In acetonitrile purified along the adopted by the authors general procedure [10] (Table 1, entry 1), we obtained the value of the rate constant somewhat lower than was found in [8], $k = 12.3\times10^6$ s^{-1}. In acetonitrile "Spectroscan" with water content less than 6×10^{-4} M the rate constant is significantly lower (entry 2), although we did not undertake any special measures for the protection from the air moisture. On the contrary, in acetonitrile "Spectroscan" with water added to the concentration 4.5×10^{-2} M the rate constant was slightly higher than in the solvent purified by the usual procedure (entry 3). In order to standardize the experimental conditions, we performed all further experiments in acetonitrile "Spectroscan" with water added to 4.5×10^{-2} M, because the water concentration of $(4–5)\times10^{-2}$ M was suggested in [10] as "normal" for the kinetic experiments.

Influence of substituents and salt additives on the reaction of triphenylverdazyls with acids in acetonitrile. If the indicator reacts with the acid resulting from the substrate solvolysis, it is necessary to know the stoichometry of this process. Triphenylverdazyl is known to react with strong acids rapidly and quantitatively in aqueous-organic solvents according to Eq. (2) [11]. But it was not known whether this holds true in aprotic solvents with low water content and in the presence of salts. We studied the effect of addition of 3×10^{-2} M (as in [8]) triethylbenzylammonium chloride (Et_3BnNCl), tetraethylammonium chloride (Et_4NCl), and tetraethylammonium bromide (Et_4NBr) on the reactions of triphenylverdazyl **Ia** and 3-(4-nitrophenyl)-1,5-diphenylverdazyl **Ib** with picric, hydrochloric, and *p*-toluenesulfonic acids in acetonitrile.

In the absence of salts and in the presence of Et_4NBr both indicators react quantitatively with acids (Fig. 1, curve *1*). However, in the presence of salts with the chloride anion the verdazyl consumption is significantly lower than the stoichiometric, and therefore we deal with an equilibrium reaction. Apparently, in this case the acidity of the medium decreases due to the complexation of protons with chloride ions, whose basicity is higher than that of bromide ions.

The equilibrium consumption of the indicator in the presence of chloride ions does not depend on the nature of the acid and the structure of the tetraalkylammonium cation of the added salt (Fig. 1, curve *2*), however, it depends on the initial concentration of the indicator (Fig. 1, curves *2* and *3*). As expected, the equilibrium in the case of nitro verdazyl **Ib** under these conditions is shifted to the left due to lower basicity of the indicator (Fig. 1, curve *4*).

We were unable to find an analytical expression for the equilibrium constant ensuring the independence of its calculated values of both the concentration of added acid and the initial concentration of the indicator. Apparently, the complexity of the observed dependence is due to the association processes (binding of ions in the conglomerates, dimerization of acid, etc.).

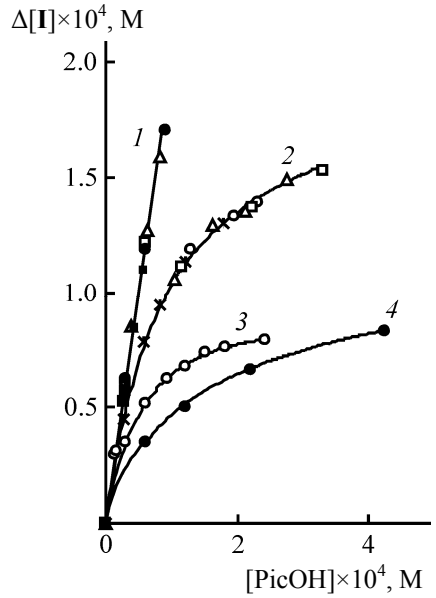


Fig. 1. The dependence of the indicator consumption on the concentration of added acid in acetonitrile at 25°C, $[H_2O]$ = 4.5×10^{-2} M. (*1*) **Ia**, PicOH, without salt (○); **Ia**, PicOH, Et_4NBr (□); **Ia**, HCl, without salt (Δ); **Ib**, PicOH, without salt (●); **Ib**, PicOH, Et_4NBr (■). (*2*) $[\mathbf{Ia}]_{init}$ = 2.31×10^{-4} M, PicOH, Et_3BnNCl (*); PicOH, Et_4NCl (○); TsOH, Et_3BnNCl (□); HCl, Et_3BnNCl (Δ). (*3*) $[\mathbf{Ia}]_{init}$ = 1.16×10^{-4} M, PicOH, Et_3BnNCl; (*4*) $[\mathbf{Ib}]_{init}$ = 2.96×10^{-4} M, PicOH, Et_3BnNCl.

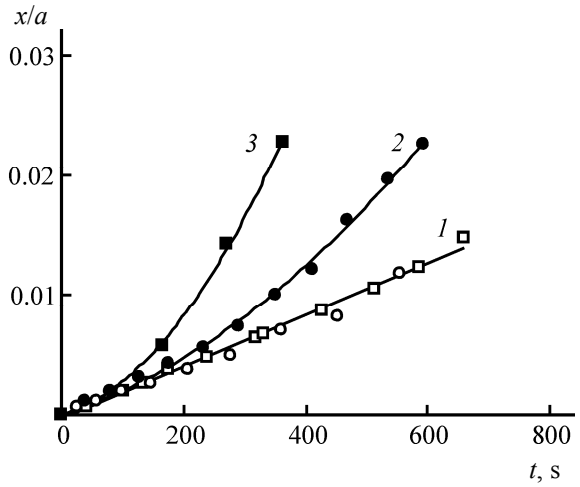


Fig. 2. Kinetics of heterolysis of 1-AdOPic in the presence of 3×10^{-2} M Et_3BnNCl in acetonitrile at 25°C, $[H_2O]$ = 4.5×10^{-2} M: (*1*) $[\mathbf{Ia}]_{init}$ = 1.16×10^{-4} M (○); $[\mathbf{Ia}]_{init}$ = 2.32×10^{-4} M (□); (*2*) $[\mathbf{Ib}]_{init}$ = 2.96×10^{-4} M; (*3*) $[\mathbf{Ib}]_{init}$ = 2.97×10^{-4} M, $[PicOH]_0$ = 9.05×10^{-4} M.

Kinetics and distribution of reaction products. To calculate the yield of picric acid in the presence of chlorides, we used the curves *2–4* (Fig. 1) as calibration plots. The kinetic graphs thus obtained for the reaction in the presence of **Ia** are nearly linear (Fig. 2, curve *1*), i.e. the observed rate constant is independent of the indicator concentration. In the case of **Ib** the rate constant tends to increase during the process (Fig. 2, curve *2*). We suppose that this is due to the autocatalytic effect of free picric acid that accumulates in the reaction mixture because of low basicity of the indicator. This is confirmed by the increase in the reaction rate in the presence of added picric acid (Fig. 2, curve *3*).

Assuming that the catalytic process is first order with respect to the acid, the system can be described by the differential Eq. (3), integration of which gives Eq. (4):

$$(dx)/(dt) = [k_0 + k_a(x + c_{HX0})]a, \quad (3)$$

$$x/(at) = k_0 + k_a[(\int_0^t xdt)/t]. \quad (4)$$

where $x = c_{HX} - c_{HX0}$ is the reaction yield, k_0 and k_a are the rate constants of non-catalytic and catalytic processes, respectively.

The regression in the appropriate coordinates (Fig. 3) gives the value of non-catalytic rate constant.

Table 2 shows that the rate constant for the heterolysis of 1-adamantyl picrate does not depend on the indicator concentration and structure both in the absence and in the presence of chloride ions. Triethylbenzylammonium chloride exhibits a positive salt effect. The contribution of the alkylation pathway in all cases is minor. Thus, both the kinetics and the products distribution in the studied reactions confirm that the verdazyls react with the acid released in the course of the substrate solvolysis.

It is noteworthy that in most cases mentioned in the review papers [2, 7] for the substrates RX the dependences of the rate of indicator consumption on its concentration and structure were observed specifically in the presence of salts with the chloride anion, and these dependences showed a "normal" behavior (increase in the reaction rate with increasing the indicator concentration and basicity). Probably, these results originate from the effect we have found in the present study. In principle, some other salts also may produce similar effects, and the effect of a specific salt may be substantial or not depending on the solvent. Thus, the mentioned above results need to be revised.

The origin of the "anomalous" dependences, when the reaction rate depends on the indicator structure in a different order or it depends either on the indicator concentration or on its structure only, remain unclear. Such dependences were usually observed in the relatively slow reactions and/or in the solvents that are difficult to purify or to monitor their purity (e.g., heterolysis of 1-adamantyl iodide in γ-butyrolactone). In these cases there exists an enhanced probability of obtaining the incorrect results due to side reactions. For example, we were not able to get any reproducible results when studying the kinetics of the heterolysis of 1-adamantyl iodide in γ-butyrolactone in the presence of **Ib**, despite repeated purification of the solvent.

We wish to emphasize again that in order to obtain the reliable kinetic results, one needs to carefully check the stoichiometry of the indicator interaction with the acid and the stability of the optical density of the resulting mixture during the appropriate time. In the experiments on the product distribution, the degree of the indicator regeneration after its reaction with acid must be checked. Our observations show that if the mixture is kept for longer times (above 15–20 min) before the addition of the reducing reagent, the degree of the triphenylverdazyl regeneration tends to fall. This is equivalent to false "increase" in the contribution of the alkylation pathway (2). We did not evaluate the significance of this effect, since the calculated contribution of the alkylation pathway in our case was small even without taking it into account. In fact, the alkylation reaction in our kinetic experiments apparently did not practically occur.

Anyway, the "abnormal" results for the substrates RX are rare and they cannot serve as a basis for the approval of the hypothesis of the applicability of triphenylverdazyls as indicators for the solvent-separated ion pairs.

EXPERIMENTAL

Adamantyl picrate [12], triphenylverdazyl **Ia** and 3-(4-nitrophenyl)-1,5-diphenylverdazyl **Ib** [13] were synthesized according to published procedures. The purity of the substrate was monitored by ^{1}H NMR spectroscopy ($CDCl_3$). For kinetic experiments acetonitrile "Spectroscan" (Labscan) was used without further purification, and some experiments were carried out in analytical grade acetonitrile purified according to [10]. Propylene carbonate (Acros, 99.5%) was kept for several months over BaO and distilled *in vacuo*. Photometric measurements were carried out on a KFK-3 spectrocolorimeter in the temperature-controlled cells with the optical length of 1 cm.

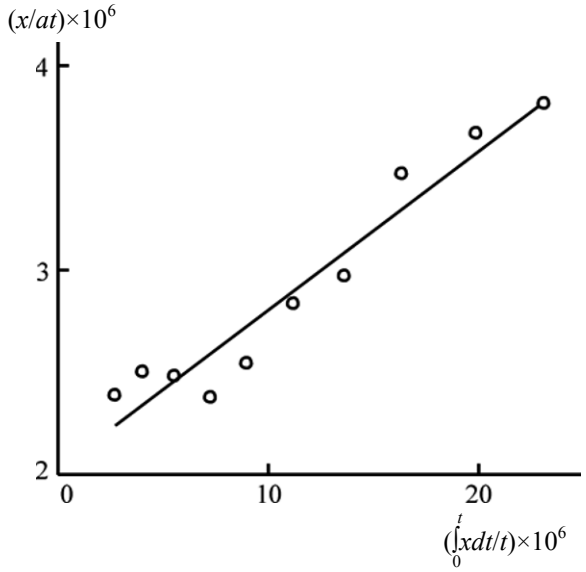


Fig. 3. Plot of dependence according to Eq. (5) for the heterolysis reaction of 1-AdOPic in acetonitrile at 25ºC in the presence of compound **Ib** at $[Et_3BnCl] = 3\times10^{-2}$ M and $[H_2O] = 4.5\times10^{-2}$ M.

Study of the reactions equilibria and kinetics. Standard solutions of picric and *p*-toluenesulfonic acids in acetonitrile were prepared from precisely weighed samples. Hydrochloric acid solution was prepared in propylene carbonate by dilution of 1 M aqueous solution (the solution of hydrochloric acid in acetonitrile is not enough stable). The amounts of the solutions added to the photometric cell were monitored by weighing to ensure the accuracy of dozing. Optical density was measured at 720 nm for **Ia**, 730 nm for **Ib**,

Table 2. Rate constants and product distribution of 1-AdOPic heterolysis in the presence of 3×10^{-2} M of Et_3BnNCl in acetonitrile at 25ºC, $[H_2O] = 4.5\times10^{-2}$ M

Indicator	$c_{init}\times10^4$, M	$k\times10^5$, s^{-1}	Contribution of flow alkylation %
Ia	2.31	2.05±0.01	14
Ia	1.16	1.99±0.02	12
Ib	2.97	2.0±0.2[a] $n = 10$, $r = 0.966$	1

[a] Calculated by Eq. (5).

and 540 nm for triphenylverdazylium salt [14]. In experiments with **Ib** the concentration of its salt was not measured because of the strong absorption of **Ib** in this area.

The kinetic experiments were carried out as described in [3]. The first order rate constant in the presence of chlorides was calculated by formula (5)

$$k = x/(at) = (c_{HX} - c_{HX0})/(at), \quad (5)$$

where x – yield of the reaction, c_{HX} and c_{HX0} – current and initial concentrations of acid, respectively, determined from the calibration graphs, a – substrate concentration, t – reaction time.

In other cases $x = \Delta[\mathbf{I}]/2$ was taken, in accordance with the stoichiometry of reaction (2). Errors are given at 95% confidence level.

The contribution of the alkylation pathway was calculated by formula (6):

$$\alpha = \frac{2(\Delta c - \Delta c_r + \Delta c_0)}{\Delta c} \times 100\%, \quad (6)$$

where $\Delta c_0 = c_{init} - c_0$ is an abrupt decrease in the verdazyl concentration after the addition of the substrate due to the free acid impurity in it, $\Delta c = c_0 - c_{min}$ is verdazyl consumption during the reaction, $\Delta c_r = c_{max} - c_{min}$ is increase in the radical concentration after the addition of the reducing reagent.

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