Russian Journal of General Chemistry, Vol. 75, No. 8, 2005, pp. 1331–1335. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 8, 2005, pp. 1402–1406.

DISCUSSIONS

Is Triphenylverdazyl an Indicator for Solvent-Separated Ion Pair?

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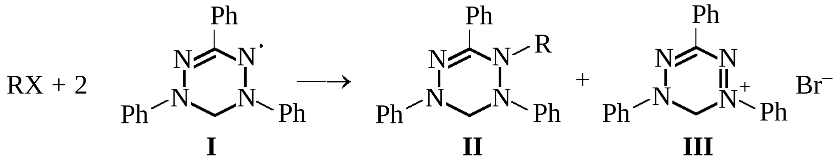
Received May 27, 2004

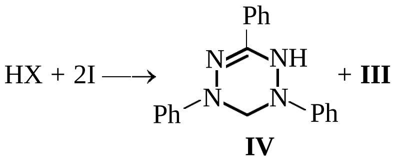
Abstract—The hypothesis implying complete capture of solvent-separated ion pairs by triphenylverdazyls used as internal indicators for unimolecular heterolysis of organic compounds was critically analyzed. Products of heterolysis of diphenylmethyl bromide in anhydrous acetonitrile in the presence of triphenylverdazyl were identified, and their distribution was determined. Alkylation of verdazyl under kinetic conditions almost does not occur, and verdazyl is consumed as a result of its reaction with hydrogen bromide liberated during the solvolysis.

G.F. Dvorko and co-workers [1, 2] advanced a hypothesis according to which triphenylverdazyl (**I**) in aprotic solvents completely traps solvent-separated ion pairs formed by heterolytic dissociation of organic substrates; therefore, it can be used as internal indicator for the rate of formation of ion-pair intermediates. This statement was put as the basis for detailed interpretation [3, 4] of extensive experimental data on salt effects in heterolytic reactions; in particular, the authors elucidated the mechanism of "negative special salt effect" and substantiated the occurrence on the reaction coordinate of an additional intermediate, space-separated ion pair.

In the general case, triphenylverdazyl is capable of concurrently reacting with the substrate and acid formed by hydrolysis of the substrate with traces of water present in the solvent [reactions (1) and (2)] [5]. Therefore, the proposed concept requires at least that the contribution of alkylation in kinetic experiments be predominating and that external solvent-separated ion pair return be absent.



(1)



(2)

These conditions imply an extremely high reactivity of verdazyl toward solvent-separated ion pair. To successfully compete with traces of water, the activity of triphenylverdazyl in unimolecular reaction with diphenylmethyl chloride should exceed the activity of azide ion in the same reaction by almost two orders of magnitude [2], whereas chloride ion (and hence azide ion) under these conditions combines with carbocationic intermediates derived from diphenylmethyl chloride at a diffusion rate [6]. Furthermore, according to the data of [7, 8], the rate constant for external return of the solvent-separated ion pair formed from

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diphenylmethyl chloride in acetonitrile exceeds 10^8 s^{-1}.[1] Complete capture of that intermediate by triphenylverdazyl (at a typical concentration of 10^{-4} M) requires the corresponding rate constant to be about 10^{13} mol^{-1} s^{-1}. However, the diffusion limit for reactions of neutral amines with cationic species derived diphenylmethyl chloride in acetonitrile is 5± 10^9 mol^{-1} s^{-1} [10]. Such values of rate constants are unprecedented for reactions involving outer-sphere electron transfer in nonstructurized systems. Taking into account that reaction of triphenylverdazyl with solvent-separated ion pair is a multistep trimolecular process [4], the above value seems to be especially surprising.

The arguments given by the authors in support to the proposed theory for substrates like RX may be grouped into three categories.

(1) Alkylverdazyls **II** were isolated in preparative experiments performed with diphenylmethyl and 1-adamantyl systems [5, 9, 11]. However, this fact does not prove their quantitative (or even predominant) formation in kinetic experiments where the concentration of triphenylverdazyl was lower by about three orders of magnitude.

(2) The relative contributions of reactions (1) and (2) were estimated [2, 9] by kinetic experiments in moist acetonitrile ([H_2O] = 0.13–0.3 M). The calculation procedure was based on the fact that addition of an alkaline reducing agent to reaction mixture promotes quantitative transformation of all products, except for alkylverdazyl, into the initial radical. Incomplete regeneration of triphenylverdazyl indicates formation of alkylation product, and the ratio of the yields (or concentrations) of compounds **II** and **IV** is proportional to the concentration ratio of the corresponding reagents ([**I**]/[H_2O]) [9]. Unfortunately, the authors did not perform experiments to estimate product distribution in anhydrous solvents used in kinetic measurements. Instead, they automatically concluded that in all aprotic solvents (as well as in the presence of any salt), the hydrolysis process is ruled out regardless of the verdazyl structure and concentration.

(3) In some reactions carried out in the presence of salts, the reaction rate depended on the concentration of verdazyl and substituents in the benzene rings of the latter (see, e.g., [12, 13]). This means that verdazyl is involved in the process at the rate-determining stage, i.e., it reacts with the substrate rather than with acid. Despite its persuasiveness, the above argument is nevertheless indirect; and it may be proved or disproved by direct experiments. Had the authors proved that alkylation products either would not have formed or would have formed in minor amounts (assuming that they are stable under the given conditions), an alternative interpretation of the observed kinetic effects should be sought for.

We believe that serious counterarguments force the proposed theory to be substantiated more rigorously. Here, the key problem is product distribution in reactions (1) and (2) under kinetic conditions. We performed experiments which allowed us to directly identify products of heterolysis of diphenylmethyl bromide in the presence of triphenylverdazyl and elucidate their distribution in anhydrous acetonitrile ([H_2O] ≤ 5 ± 10^{-2} M) where (in keeping with the conclusions drawn in [2]) hydrolysis of the substrate almost does not occur.

Identification of the products. Treatment of compounds **II** (R = Ph_2CH) and **IV** with nitric acid leads to formation of intensely colored salt **III**, and they are readily determined by thin-layer chromatography at a concentration of 10^{-4} M (R_f = 0.62, 0.38, and 0, respectively: silica gel/benzene). The reaction of HBr with triphenylverdazyl (2 ± 10^{-4} M) afforded compounds **III** and **IV** [according to scheme (2)]. In the reaction of triphenylverdazyl with diphenylmethyl bromide, performed under the same conditions, no product **II** was detected in the reaction mixture even after fivefold application to a chromatographic plate. Instead of **II**, we identified leucoverdazyl **IV**. Some difficulties in the analysis of the reaction mixture arose from the fact that compound **IV** applied to the start line underwent fast oxidation to the corresponding salt on drying. A freshly prepared solution of a mixture of leucoverdazyl with diphenylmethyl bromide behaved similarly, whereas pure leucoverdazyl remained unchanged upon drying on silica gel.

Distribution of the products. As stated in [2], verdazyl is completely regenerated from a mixture of its salt and leuco base by the action of an alkaline formaldehyde solution. This statement was based on the data of [14], where the regeneration was effected in a 3 : 1 acetonitrile–water mixture. Our results are approximately similar (Table 1, run nos. 1, 2). However, complete recovery of triphenylverdazyl after its reaction with HCl cannot be achieved using the same reagent in acetonitrile with a lower concentra-

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[1] There are also other methods for estimation of the same quantity; however, discussion on this topic goes beyond the scope of the present article. Even though the rate constant for external solvent-separated ion-pair return amounts to ca. 10^6 s^{-1} [9], the rate constant for its capture by triphenylverdazyl should exceed the diffusion limit by an order of magnitude.

Table 1. Regeneration of triphenylverdazyl from products of its reaction with HCl and from verdazylium bromide (**III**) in acetonitrile at 25°C[a]

Run no.	Reducing agent[b]	$c_{\text{init}} \times 10^4$, M	$c_{\text{min}} \times 10^4$, M	$c_{\text{max}} \times 10^4$, M	β[c]
Triphenylverdazyl (**I**) + HCl					
1[d]	A	1.13	0.26	1.07	0.93
2[d]		1.07	0.26	1.02	0.93
3		1.32	0.23	1.13	0.83
4		1.18	0.32	0.85	0.63
5		1.00	0.23	0.74	0.67
6		1.28	0.45	0.95	0.58
7		1.13	0.15	0.72	0.58
8	B	1.54	0.02	1.48	0.96
9		1.39	0.05	1.36	0.99
Triphenylverdazylium bromide (**III**)					
10	A	0.85	–	0.85	1.00
11		1.27	–	1.27	1.00
12	B	1.19	–	1.19	1.00

[a] For denotations, see Experimental. [b] Reducing agents: a mixture of equal volumes of 2 N aqueous NaOH and 37% formaldehyde solution (A) and a solution of 33% of *N*,*N*-dimethyl-*p*-methoxyaniline and 10% of *N*-methylmorpholine in acetonitrile. [c] β is the degree of regeneration of compound **I**; in experiments with HCl, $\Delta c_r/(c_{\text{init}} - c_{\text{min}})$. [d] In acetonitrile–water (3 : 1, by volume).

tion of water (run nos. 3–7), while pure verdazilium salt is quantitatively reduced to the radical (run nos. 10, 11). Thus the degree of regeneration of triphenylverdazyl from products of reaction (2) by an alkaline solution of formaldehyde tends to decrease as the concentration of water in the solvent decreases. Neglect of this factor is likely to be responsible for erroneous conclusions drawn in [2, 9].

We measured the rate constant for heterolysis of diphenylmethyl bromide. The obtained value was very consistent with the rate constant 1.86×10^{-7} s^{-1} [5] in acetonitrile containing much less than 0.05 mol/l of water. After addition of an alkaline formaldehyde solution to the reaction mixture (Table 2; run nos. 1–3), the degree of regeneration of verdazyl was approximately the same as in the reaction of **I** with HCl, which indicated the absence or insignificant contribution of the alkylation process. However, poor reproducibility of the results under these conditions did not allow us to estimate the relative contributions of reactions (1) and (2) with an acceptable accuracy.

In order to raise reliability of the results, it would be desirable to carry out analogous experiments with a reducing agent ensuring complete regeneration of verdazyl from both its salt and products of its reaction with HCl. Satisfactory data were obtained with the use of a solution of 33% of *N*,*N*-dimethyl-*p*-methoxyaniline and 10% of *N*-methylmorpholine in acetonitrile (the solution was added in an amount of 50 μl per 2 ml of the reaction mixture; Table 1, run nos. 8, 9, 12). Special photometric experiments showed that compound **II** was not converted into the radical species under these conditions. The results obtained with the above reducing agent (Table 2; run nos. 4, 5) unambiguously indicated that verdazyl did not capture all solvent-separated ion pairs derived from diphenylmethyl bromide and, moreover, that its alkylation is not the major process.

Thus, under the conditions of kinetic experiments with diphenylmethyl bromide in anhydrous acetonitrile in the absence of salts, almost no alkylation products are formed from triphenylverdazyl. Therefore, the hypothesis implying complete capture of solvent-separated ion pairs under these conditions is invalid. This hypothesis should be verified by experiments performed in other solvents, as well as under the conditions under which the reaction rate depends on the radical concentration and structure.

EXPERIMENTAL

Diphenylmethyl bromide [15], triphenylverdazyl, triphenylverdazylium bromide [16], leucoverdazyl

Table 2. Distribution of heterolysis products of diphenylmethyl bromide (c = 0.02 M) in the presence of triphenylverdazyl in acetonitrile at 25°C[a]

Run no.	Reducing agent	$c_{\text{init}} \times 10^4$, M	$c_0 \times 10^4$, M	$c_{\text{min}} \times 10^4$, M	$c_{\text{max}} \times 10^4$, M	β[b]	α[c]	$k \times 10^6$, s^{-1}
1	A	1.07	1.05	0.23	0.91	0.81		2.15 ± 0.03
2		1.15	1.09	0.23	0.97	0.79		2.14 ± 0.04
3		1.20	1.14	0.23	0.88	0.65		2.31 ± 0.04
4	B	1.15	1.09	0.23	1.07	0.91	0.13	1.96 ± 0.02
5		1.68	1.53	0.23	1.54	0.89	0.16	2.08 ± 0.04

[a] For denotations of reducing agents and concentrations, see notes [a], [b] to Table 1. [b] $\beta = (\Delta c_r - c_0)/\Delta c$. [c] Calculated by formula (3).

[17], and alkylverdazyl (**II**, R = Ph_2CH) [5] were prepared by known procedures. Diphenylmethyl bromide was purified by vacuum distillation. The melting points and spectral parameters of the compounds were in agreement with those reported in the literature. Acetonitrile was distilled over P_2O_5 and, just before use, over CaH_2.

The ^{1}H NMR spectrum of compound **II** was recorded on a Gemini-200 spectrometer (200 MHz) in $CDCl_3$, δ, ppm: 2.98 d (1H, CH_2, J = 11.8 Hz), 5.03 d (1H, CH_2, J = 11.8 Hz), 6.09 s (1H, CH), 7.75–6.60 m (23H, H_{arom}), 7.9 m (2H, H_{arom}).

Photometric measurements were performed on a KFK-3 photometer using 1-cm cells: **I**, λ = 720 nm, ε = 4330; **II**, λ = 540 nm, ε = 12 170 [1]. Thin-layer chromatography was performed on Silicagel-60 F254 (Riedel-de Haën); layer thickness 0.2 mm; eluent benzene;[2] the chromatograms were developed by treatment with nitric acid vapor for a short time.

Chromatographic analysis of the reaction mixtures. Two samples were applied on the start line of a plate with a size sufficient for parallel elution of four samples, and the plate was eluted without drying of the samples. The plate was dried, and the band containing sample no. 1 was cut off and developed. The position of the violet spot was assigned the new start line on the remaining plate, solutions of authentic samples of **II** and **IV** were applied on the new start line, and the plate was eluted and developed in a usual manner.

Procedure for photometric measurements. A weighed sample of a substrate or 1–2 drops of a dilute aqueous solution of hydrogen chloride was added to a solution of triphenylverdazyl in a cell maintained at a constant temperature. The mixture was kept for a required time, the reducing agent was added, and the maxiaml optical density at λ = 720 nm was measured. When a mixture of amines was used as reducing agent, the maximal yield of verdazyl was reached in 5–10 min. Dilution of the reaction mixture due to addition of reducing agent (V_{red}) was taken into account by recalculation of the measured verdazyl concentration c_{mes} to the initial volume.

$$c = c_{mes}(2 + V_{red})/2.$$

Mathematical treatment of the results. The rate constant was calculated by the equation $dc/2dt = k[RX]$. The confidence intervals were given at a probability of 95%. The contribution of the alkylation process was calculated by formula (3).[3]

$$\alpha = [2(\Delta c - \Delta c_r + \Delta c_0)]/\Delta c. \qquad (3)$$

Here, $\Delta c_0 = c_{init} - c_0$ is jumpwise decrease in the verdazyl concentration upon addition of substrate due to the presence of acid in the latter;, $\Delta c = c_0 - c_{min}$, consumption of verdazyl during the reaction, and $\Delta c_r = c_{max} - c_{min}$, increase in the verdazyl concentration upon addition of reducing agent.

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[2] We failed to detect compound **IV** in the reaction mixture by TLC on Sorbfil STKh-1VE silica gel (8–12 μm).

[3] Dvorko *et al.* [2] used a more complex but essentially equivalent formula which also implied measurement of the concentration of verdazylium salt.

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