POLAROGRAPHIC INVESTIGATION OF DONOR — ACCEPTOR
PROPERTIES OF TRIPHENYLVERDAZYLS
IN PROPYLENE CARBONATE

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The electrochemical reactions of stable radicals have been little investigated. In the literature there are data on the electrochemical oxidation and reduction of diphenylpicrylhydrazyl (DPPH) in various organic solvents [1, 2], the reduction of N-oxide radicals in water [3], and the reduction of the indophenoxyl radical in alcohol [4] and acetonitrile [4, 5]. The effect of substituents on the cathodic reduction potentials of phenoxyl radicals in acetonitrile was examined in [6], and the possibility of polarographic titration of N-oxide radicals in acidic water—acetone media was demonstrated in [7]. It was also shown that the diphenylverdazyl biradical is oxidized reversibly to the respective dication [8].

Investigation of the kinetics and mechanism of the reactions of triphenylverdazyls (RN$^\cdot$) showed [9, 10] that these stable nitrogen-containing radicals (1) can behave both as electron donors and as electron acceptors, and the effect of the substituent in the radical on the reaction rate depends largely on the nature of the reaction. To establish the significance of the donor—acceptor characteristics of the triphenylverdazyls in the mechanism of their ionic-radical transformations we studied the polarographic reduction and oxidation of substituted triphenylverdazyls in propylene carbonate. Separate experiments were also carried out with DPPH.

The polarographic measurements were made on an ON-102 instrument [11]. The mercury flow rate from the capillary was 1.16 mg/sec with t = 5 sec. A 0.05 M solution of tetraethylammonium perchlorate was used as supporting electrolyte. The reference electrode was a saturated aqueous calomel electrode. The measurements were made in a thermostated cell at 25 ± 0.1°C. The concentration of the radical in the solution was ~1 · 10^{-3} M.

To identify the products from electrochemical oxidation and reduction of triphenylverdazyl in propylene carbonate the radical was submitted to electrolysis with controlled potential (P-5827 potentiostat) in a three-electrode cell with separate cathode and anode compartments at platinum electrodes with a silver chloride electrode as reference electrode. The electrolysis was carried out in a stream of argon. The identification was realized by spectrophotometry on an SF-4 instrument.

The triphenylverdazyl radicals 1,3,5-triphenylverdazyl (H—RN$^\cdot$),1,5-diphenyl-3-(4-nitrophenyl)-verdazyl (NO$_2$—RN$^\cdot$), 1,5-diphenyl-3-(4-chlorophenyl)verdazyl (Cl—RN$^\cdot$), 1,5-diphenyl-3-(4-methoxyphenyl)verdazyl (OCH$_3$—RN$^\cdot$), 1,5-diphenyl-3-(4-acetoxyphenyl)verdazyl (CH$_3$COO—RN$^\cdot$), and 1,3-bis(4-methoxyphenyl)-5-phenylverdazyl (bis-OCH$_3$—RN$^\cdot$) were synthesized and purified according to [12, 13]. Diphenylpicrylhydrazyl was obtained according to [14]. The propylene carbonate was distilled twice under vacuum on a high-efficiency fractionating column; bp 102°C (6 mm Hg) [15].

All the triphenylverdazyl radicals and DPPH give well-defined anodic and cathodic waves of equal height, and with identical molar concentrations of the reagents the wave heights are practically identical for all the investigated radicals. If it is assumed that the diffusion coefficient of the radical in propylene

TABLE 1. Results from Polarographic Investigation of Triphenylverdazyls in Propylene Carbonate at 25°C

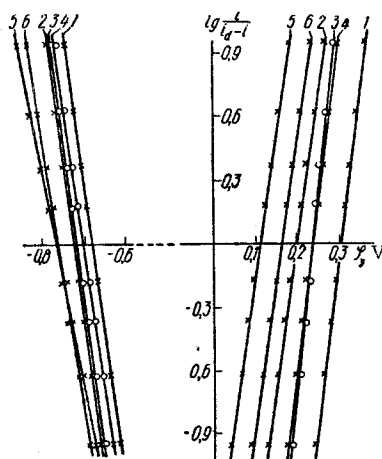| Radical	Cathodic reduction		Anodic oxidation	
	slope β, mV	$E_{1/2}$, eV	slope β, mV	$E_{1/2}$, eV
NO_2—RN·	65	—0,680	65	0,305
Cl—RN·	60	—0,720	60	0,235
CH_3COO—RN·	70	—0,710	65	0,240
H—RN·	60	—0,725	70	0,200
CH_3O—RN·	70	—0,755	75	0,165
bis-CH_3O—RN·	80	—0,770	75	0,110
DPPH	65	0,175	—	>0,500

Fig. 1   Fig. 2
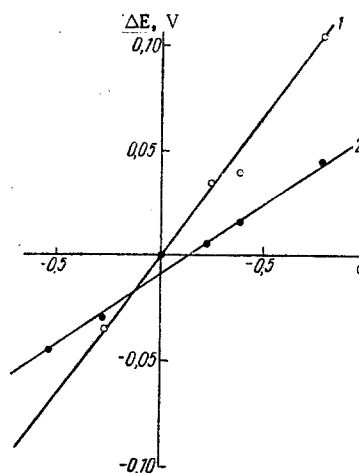
Fig. 1. Polarograms for 10^{-3} M solutions of the triphenyl-verdazyls in propylene carbonate: 1) NO_2—RN·; 2) H—RN·; 3) Cl—RN·; CH_3COO—RN·; 5) bis-CH_3O—RN·; 6) CH_3O—RN·.

Fig. 2. Dependence of $\Delta E_{1/2}$ for anodic oxidation (1) and cathodic reduction (2) of triphenylverdazyls on the Hammett σ constants in propylene carbonate.

carbonate does not depend on the nature of the substituent in the phenyl nucleus,* it can be considered that the same number of electrons is involved in the cathodic and anodic processes for all the radicals. The oxidation and reduction waves of the triphenylverdazyl radicals are closely described by the Heyrov-sky—Ilkovic equation (Fig. 1). The half-wave potentials for both waves do not depend on the concentration of the radical. The slopes of the polarograms β against semilogarithmic coordinates (Table 1) correspond to a one-electron transfer. By means of a Kalousek commutator anodic—cathodic waves were obtained for both the oxidation wave and the reduction wave.

On the basis of these data it can be concluded that electrochemical oxidation and reduction of the triphenylverdazyls takes place reversibly with transfer of one electron [16]. Similar behavior was observed for DPPH. Spectroscopic investigation of the oxidation and reduction products from H—RN· confirmed these conclusions. During oxidation of H—RN· there is a change in color; the green solution of the radical (λ_{max} =720 nm) becomes red (λ_{max} = 540 nm, formation of H—RN⁺ cation [12]). Electrochemical reduction of H—RN· in a stream of argon leads to the formation of a colorless solution (λ_{max} = 280 nm). In air the latter forms a green solution, the absorption spectrum of which corresponds to the spectrum of a solution of H—RN·. This is evidently due to the fact that the unstable triphenylverdazyl anion (not described in the literature) formed at the cathode is converted comparatively rapidly into the leuco

*Such an assumption is perfectly justified, since the dimensions of the radical depend little on the nature of the substituents employed.

base H$-$RNH ($\lambda_{max} = 300$ nm in benzene [12]), which (as known [12]) is readily oxidized to H$-$RN*. Thus, the behavior of the triphenylverdazyl radicals at the dropping mercury electrode can be described by the following scheme:

$$(X = H, OCH_3, Cl, COOCH_3, NO_2; Y = H, OCH_3). \tag{1}$$
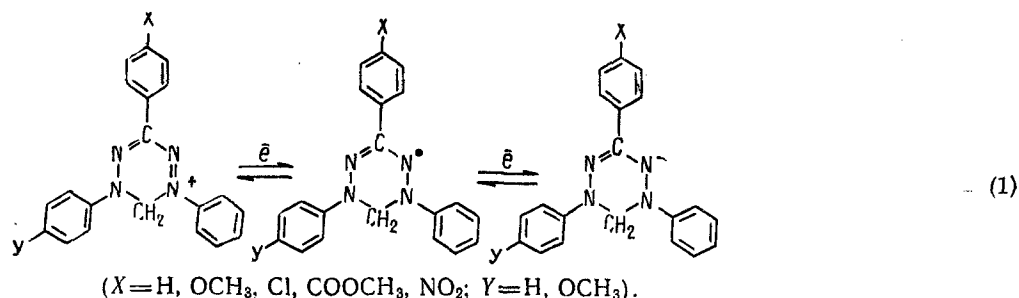
The data from the polarographic investigation of the triphenylverdazyls in propylene carbonate, presented in Table 1, show that the radicals undergo oxidation considerably more readily than reduction. It is interesting that the N-oxide radicals [3], indophenoxyl radical [5], diphenylpicrylhydrazyl [2], and the phenoxyl radicals [6] are reduced more easily than they are oxidized; i.e., these radicals are relatively strong electron acceptors. Compared with them the triphenylverdazyls, with other conditions equal, must be electron donors. From Table 1 it is seen that the anodic oxidation potentials of RN* decrease in the order

$$NO_2-RN^*, CH_3COO-RN^*, Cl-RN^*, H-RN^*, CH_3O-RN^*, \text{bis-} CH_3O-RN^*$$
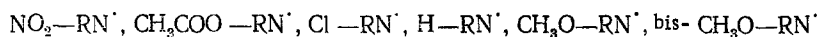
while the cathodic reduction potentials increase. In both cases the effect of the substituent is closely described by the modified Hammett equation [17]: For reduction: $\Delta E_{1/2} = E^X{}_{1/2} - E^O{}_{1/2} = 0.071 \ \sigma - 0.01V$ (r = 0.979); for oxidation: $\Delta E_{1/2} = E^X{}_{1/2} - E^0{}_{1/2} = 0.131 \ \sigma - 0.001$ V (r = 0.994), where $E^0{}_{1/2}$ is the anodic half-wave potential for H $-$ RN, $E^X{}_{1/2}$ is the same for the substituted triphenylverdazyls, and r is the correlation coefficient. The ρ_π constants of the polarographic reduction and oxidation reactions, calculated for the five monosubstituted triphenylverdazyls, are 0.071 and 0.131 V, respectively.* The ob-tained relationships are presented graphically in Fig. 2. It is interesting that the values obtained for bis-CH$_3$O$-$RN* fit well on to the correlation curves if it is assumed that $\sigma_{\text{bis-CH}_3O - RN^*} = 2\sigma_{CH_3O - RN^*} = -0.54$.

The specificity of the donor$-$acceptor characteristics of the triphenylverdazyls is evidently due to the fact that the phenyl rings of these radicals are partly withdrawn from the plane of the heterocyclic ring and form a structure of the umbrella type. Only this can explain the high dipole moment of triphenyl-verdazyl (2.94 D [12]). During the formation of the RN$^-$ anion the departure of the phenyl groups from the conjugation plane clearly increases (the umbrella closes), whereas the formation of the cation leads to the coplanar RN$^+$ ion (the umbrella opens). This is probably the reason for the fact that the electron-donating characteristics of the verdazyls depend more strongly on the nature of the substituent than the electron-accepting characteristics.

These suppositions make it possible to explain the kinetic relationships of the disproportionation of triphenylverdazyls in the presence of carboxylic acids [9]:

$$2RN^* + R'CO_2H \rightleftarrows RNH + RN^{+-}O_2CR',$$
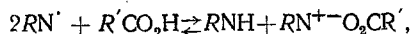
where the rate of formation of the salt in DMF is described by a quadrimolecular kinetic equation [19]

$$V = k_4 [RN^*]^2 [R'CO_2H]^2.$$

In the transition state (II) of this reaction an electron is transferred from one molecule of the radical to another:

$$\text{(II)}$$

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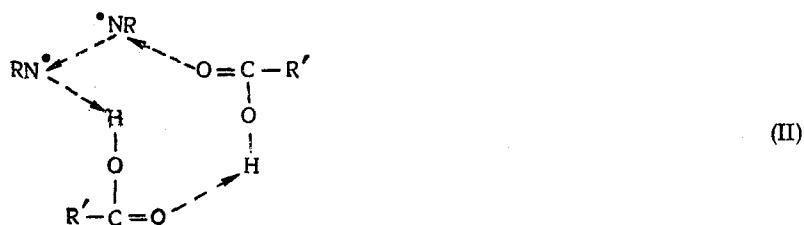
*In polarography the ρ_π values are given in volts, whereas dimensionless ρ values are used in physical organic chemistry. Conversion [18] shows that in our case $\rho = 1.19$ for reduction and $\rho = 2.20$ for oxidation.

However, this process in itself does not occur. The ESR spectrum of the mixture of triphenylverdazyls corresponds to the superimposition of the spectra of two radicals. This shows that there is no electron exchange between the radicals. Moreover, during investigation of the mechanism of the dehydrogenation of dihydropyridines with triphenylverdazyls it was shown that the triphenylverdazyl ions are not formed even when such diverse radicals as $NO_2-RN^{\cdot}$ and bis-$CH_3O-RN^{\cdot}$ are present in the solution [20]. The absence of electron transfer between the triphenylverdazyl radicals can be explained by the fact that the nonplanar molecules of the radical cannot approach each other at the required distance. Participation of two molecules of the carboxylic acid is therefore required for realization of the disproportionation of the triphenylverdazyls; the formation of the transition state (II) with participation of two $RN^{\cdot}$ molecules and two carboxylic acid molecules is the necessary mode for realization of electron transfer from one molecule of the radical to the other.

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