0.52 g of 1-methylbenzimidazole. The products were identified from the IR spectra of genuine samples.

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EPR AND POLAROGRAPHY OF NITROAZOLES.

6.* 3-NITRO-1,2,4-TRIAZOLES

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The electrochemical reduction of eight 3-nitro-1,2,4-triazole derivatives in acetonitrile was investigated by polarography and EPR spectroscopy.

We have previously shown that N-unsubstituted 5(3)-substituted derivatives of 3(5)-nitro-1,2,4-triazole are reduced in acetonitrile in two formally one-electron steps to stable dianion radicals (DAR), which are recordable in the EPR spectra [2].

However, the literature contains no information regarding the electrochemical behavior of dinitrotriazoles in aprotic media. In this connection, we undertook a study, by EPR spectroscopy and polarography, of the mechanism of the electrochemical reduction (ECR) in acetonitrile of dinitro-1,2,4-triazole derivatives I-III and model compounds IV-VIII.

The presence of two-nitro groups in the molecule substantially changes the polarographic behavior of I as compared with the behavior of its mononitro analog VII. Three waves are observed in the polarogram of 3,5-dinitro-1,2,4-triazole; the reduction is facilitated to such an extent that the first irreversible wave is observed at positive potentials (Table 1 and Fig. 1). Its intensity with respect to the current is markedly depressed and corresponds to the transfer of ~0.5 of an electron. The second wave has split character, and its overall current corresponds to an approximately one-electron level. The third wave is a multi-electron wave (virtually eight times higher than the first wave) and corresponds formally to the transfer of 4.4 electrons per molecule. Two different signals were recorded in the EPR spectra in the electrochemical reduction of I. The first signal shows up at the potentials of the second wave with a hyperfine structure (hfs) corresponding to coupling of an unpaired electron with five nitrogen atoms and to a symmetrical distribution of the spin density (Tables 1 and Fig- 2a). When the potential is increased to the values of the third wave, the indicated EPR signal vanishes, and another signal, the hfs of which corresponds to coupling of an unpaired electron with four nitrogen atoms (Table 1 and Fig. 2b), arises in place of it.

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*See [1] for communication 5.

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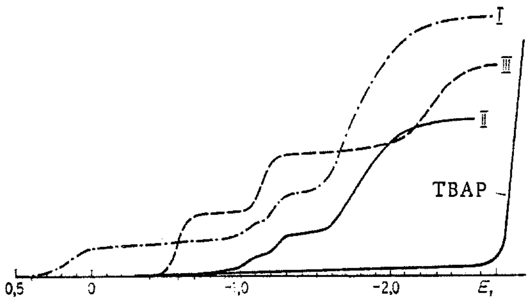
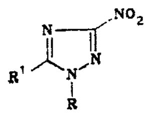
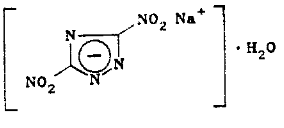


Fig. 1. Polarograms of 3-nitro-1,2,4-triazoles I-III and tetra-n-butylammonium perchlorate (TBAP).

It should be noted that the liberation of microscopic gas bubbles can often be observed in the electrochemical reduction of N-unsubstituted nitroazoles. Gas evolution was not observed in the reduction of their N-methyl derivatives under identical conditions.



I, III–VIII



II

I R=H, $R^1=NO_2$; III R=CH_3, $R^1=NO_2$; IV R=H, $R^1=NH_2$; V R=H, $R^1=N(CH_3)_2$; VI R=CH_3, $R^1=NH_2$; VII R=R^1=H; VIII R=CH_3, R^1=H

Taking into account data on the reduction of N-unsubstituted nitroazoles [2-4], we assigned the EPR signal corresponding to a symmetrical distribution of the spin density (Fig. 2a) to dianion radical IX. The correctness of this assignment is confirmed by the recording of the same EPR signal in the electrochemical reduction under identical conditions of 3,5-dinitro-1,2,4-triazole sodium salt (II), which dissociates in solution; the dinitro-1,2,4-triazole anion is reduced in the first step of the reaction (see Scheme 1). The polarograms of I and II differ only with respect to the presence of the first wave in the region of positive potentials (Fig. 1).

The known mechanism of a reaction of the "father-with-son" type [5, 6], in which the primary anion radical (AR) reacts with the starting compound with the formation of a neutral radical and an anion, evidently cannot explain the observed depression of the height of the first wave in the reduction of I, since it is substantially greater than this mechanism suggests [6]. A comparison of the results of the reduction of I and II makes it possible to assume that 3,5-dinitro-1,2,4-triazole undergoes significant dissociation in the near-electrode space (its pK_a in water is −0.66 [7]), and undissociated dinitro-1,2,4-triazole molecules are reduced at positive potentials. The splitting of the second reduction wave of I and of the identical-to-it first wave of its sodium salt II, which depends on the concentration of the starting depolarizer, is evidently due to the reduction at somewhat different potentials of the adsorbed and nonadsorbed anions. (The overall heights of these waves correspond to an approximately one-electron level.) However, according to the mechanism of a reaction of the "father-with-son" type, the height of the second wave should be approximately equal to the height of the first wave [6]. Moreover, the indicated mechanism is not applicable to the reduction of the dinitro-1,2,4-triazole sodium salt. Thus, the

Scheme 1

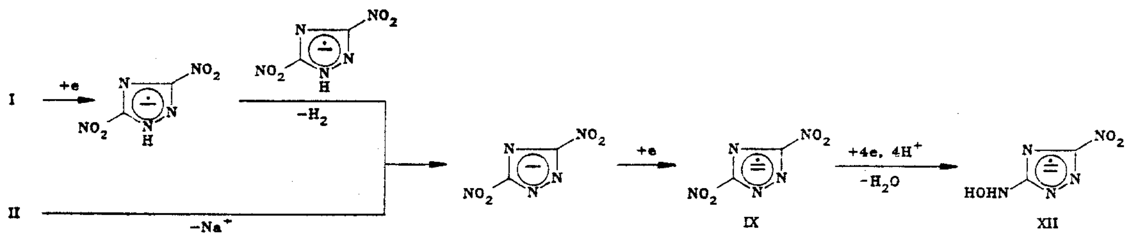
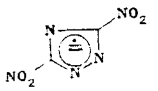
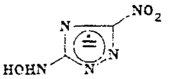
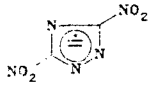
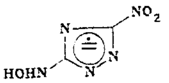
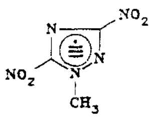
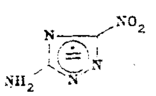
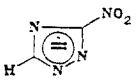
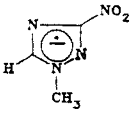


TABLE 1. Results of Polarographic and EPR Studies of Nitro Derivatives of 1,2,4-Triazole

Compound	$E_{1/2}$, V	n[a]	Reduction product recorded in the EPR spectrum	Character of the hfs of the observed EPR signal	hfs constants calc. with a computer, mT				
					$a_N^{NO_2}$	$a_N^{NO_2}$	a_N	a_N	a_N
I	+0,17	0,53	—	—	—	—	—	—	—
	−0,98 −1,17	1,00		$5_N^{NO_2}\times 3_N\times 5_N$	0,632	0,632	0,214	0,038	0,038
	−1,72	4,40		$3_N^{NO_2}\times 3_N\times 3_N\times \times 3_N$	1,522	—	0,265	0,105	0,097
II	−0,99 −1,21	0,90		$5_N^{NO_2}\times 3_N\times 5_N$	0,632	0,632	0,214	0,038	0,038
	−1,71	3,60		$3_N^{NO_2}\times 3_N\times 3_N\times \times 3_N$	1,522	—	0,265	0,105	0,097
III	−0,55	1,10	—	—	—	—	—	—	—
	−1,11	1,00	—	—	—	—	—	—	—
	−2,23	1,12		$3_N^{NO_2}\times 3_N^{NO_2}\times 3_N\times \times 3_N\times 4_H^{CH_3,b}\times \times 3_N$	1,302	0,250	0,176	0,154	0,046
IV	−1,02	0,65	—	—	—	—	—	—	—
	−1,86	0,78		$3_N^{NO_2}\times 3_N\times 3_N\times \times 3_N$	1,520	—	0,260	0,100	0,087
V	−1,03	0,63	—	—	—	—	—	—	—
	−1,78	0,75		$3_N^{NO_2}\times 3_N\times 3_N\times \times 3_N$	1,536	—	0,265	0,105	0,087
VI	−1,09	1,03	—	—	—	—	—	—	—
	−2,38	2,96	—	—	—	—	—	—	—
VII	−0,77	0,89	—	—	—	—	—	—	—
	−1,65	0,97		$3_N^{NO_2}\times 2_H{}^{c}\times \times 3_N\times 3_N\times 3_N$	1,410	—	0,167	0,033	0,030
VIII	−1,15 −2,67	1,02 2,80		$3_N^{NO_2}\times 2_H{}^{d}\times \times 3_N\times 3_N\times 3_N\times \times 4_H^{CH_3,e}$	1,160	—	0,150	0,110	0,100

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[a] The apparent number of electrons calculated relative to the first wave of nitrobenzene.
[b] Constant $a_H^{CH_3} = 0.136$ mT.
[c] Constant $a_H = 0.198$ mT.
[d] Constant $a_H = 0.460$ mT.
[e] Constant $a_H^{CH_3} = 0.020$ mT.

peculiarities of the reduction of II and 3,5-dinitro-1,2,4-triazole (I) itself provide evidence that the latter is reduced in the first two steps to a dianion radical (Scheme 1). A bimolecular mechanism of the reaction of the primary anion radicals of N-unsubstituted nitroazoles, which is accompanied by the liberation of molecular hydrogen, is evidently the

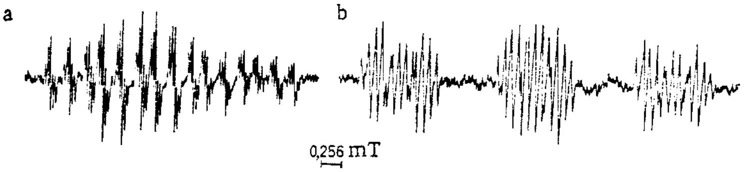


Fig. 2. EPR signals recorded in the electrochemical reduction of 3,5-dinitro-1,2,4-triazole (I) and its sodium salt (II): a) at —1.2 V; b) at —1.8 V.

most likely mechanism [8] and has been demonstrated by the method of a rotating disk electrode with a ring for nitrobenzimidazoles [1].

The subsequent reduction of dianion radicals IX, formed in the electrochemical reduction of I and II, is realized at potentials on the order of —1.7 V and requires more detailed examination. With respect to their characteristics, the EPR signals observed in this case (Fig. 2b) virtually coincide with the signals of the dianion radicals of 3(5)-nitro-5(3)-amino-1,2,4-triazole (X) and 3(5) nitro-5(3)-dimethylamino-1,2,4-triazole (XI) (Table 1). However, the polarographic data provide evidence that dianion radical XI takes on only four more electrons, thereby undergoing reduction to dianion radical XII (see Scheme 1). The close values of the hfs constants of dianion radicals X-XII are due to the similar electron-donor properties of the amino-dimethylamino, and hydroxylamino groups [9].

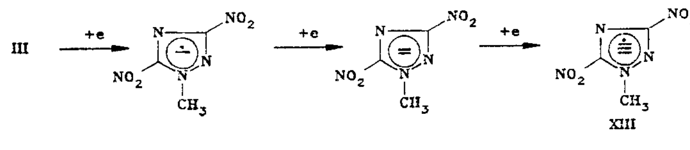
Thus an imine proton may serve as the source of protons in the reduction of the nitro group to a hycroxylamino group in I in thoroughly purified acetonitrile, and hydrate water may serve as the source in the case of the dinitro-1,2,4-triazole sodium salt II.

In this connection, it seemed of interest to study the electrochemical behavior under identical conditions of the N-methylated derivative (III) of 3,5-dinitro-1,2,4-triazole, in which an NH proton is absent. Three one-electron waves are observed in the polarogram of this compound; the first two waves are reversible, and the third wave is a gently sloping wave in the vicinity of the inert electrolyte discharge (Table 1 and Fig. 1). We were able to record an EPR signal only at the potentials of the third wave. The character of its hfs is due to coupling of an unpaired electron with five nitrogen atoms and three equivalent protons (Table 1), i.e., the structure of the resulting free radical corresponds to the starting compound. However, the hfs constant of the nucleus of the nitrogen atom of the nitro group for the primary anion radical of III should be much smaller than in the case of the anion radical of the mononitro derivative VIII corresponding to it (Table 1).

The linearization of the first wave in coordinates $\log \frac{i^{2/3}}{i_{\lim} - i}$ and E constitutes evidence for fast reactions involving dimerization of the primary anion radicals. This is evidently why the primary anion radicals of 1-methyl-3,5-dinitro-1,2,4-triazole cannot be recorded by EPR spectroscopy in the electrochemical cell with a stationary mercury drop. At the potentials of the second wave the primary anion radicals are reduced to diamagnetic dianions. Transfer of a third electron to the molecule at the potentials of the third wave corresponds to the formation of a trianion radical (XIII).

Thus the absence of an imine proton in III makes more pronounced reduction of the nitro group impossible in an aprotic medium. It is curious to note that EPR signals are not recorded at all in the electrochemical reduction of 1-methyl-3-nitro-5-amino-1,2,4-triazole (VI), although judging from the polarogram (see Table 1: two waves, the first of which is a one-electron wave, and the second of which is a three-electron wave), reduction should proceed as in the reduction of nitrobenzene and VII. However, the first one-electron wave

Scheme 2



(2)

is linearized only in coordinates of $\log \frac{i^{3/2}}{i_{\lim}-i}$ and E, which constitute evidence for simultaneous electron transfer by a bimolecular chemical reaction [10]; this evidently prevents the accumulation of a steady-state concentration of primary anion radicals sufficient for recording by EPR spectroscopy.

EXPERIMENTAL

Nitroazoles I and III-VIII were obtained by the methods in [11-15] and were purified by vacuum sublimation immediately prior to use. The 3,5-dinitro-1,2,4-triazole sodium salt (II) was obtained and purified by the method described in [11]. The acetonitrile was purified by a modified method [16].

The polarograms were recorded with OH-102 and OH-105 polarographs (Hungary) relative to a saturated calomel electrode with tetra-n-butylammonium perchlorate as the inert electrolyte and the use of a dropping mercury electrode with forced detachment of the drop ($m^{2/3}t^{1/6} = 1.5\ mg^{2/3} \cdot sec^{-1/2}$). Freshly purified nitrobenzene was used as the standard substance. The operating depolarizer concentration was $5 \cdot 10^{-4}$ mole/liter.

Electrochemical generation of the ion radicals was realized in special electrochemical cells that had been previously deoxygenated by successive freezing and thawing of solutions in vacuo and were then filled with argon purified over potassium–sodium alloy. The EPR spectra were recorded with an RE-1307 spectrometer with stabilization of the resonance conditions. The theoretical spectra were calculated with an M4030 computer with an output to a graph plotter with allowance for the Lorentzian form of the line and an individual component width of 0.012-0.020 mT.

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