TETRAZOLE DERIVATIVES.

XVII.* POLAROGRAPHIC REDUCTION OF 2-(5-TETRAZOLYL)-3-ARYL-5-(ALKYL)ARYLTETRAZOLIUM BETAINES

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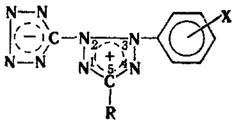
The polarographic reduction of tetrazolyl-containing tetrazolium salts with betaine structures and various substituents attached to the $C_{(5)}$ and $N_{(3)}$ atoms was investigated. It is shown that the depolarization of the tetrazolium salts proceeds in three electrochemically irreversible steps. In the first step one observes two-electron reduction to a formazan dianion without the consumption of protons. Electron-donor substituents facilitate the reduction, whereas electron-acceptor substituents hinder it. The substituent effect is manifested to a greater extent from the 3 position of the tetrazolium ring.

The diverse applications of tetrazolium salts are based mainly on their ability to undergo reduction to give formazans. This is precisely the reason for their use as indicators for various redox processes [2] and, more recently, for poisoning oxide films in the manufacture of plated integrated circuits [3].

Tetrazolium salts with heteroaromatic substituents attached to the N_2 atom are unstable in many cases and are capable of hydrolytic cleavage at the exocyclic C-N bond with splitting out of a heteryl residue [4]. Tetrazolium salts containing tetrazole substituents are prominent members of this series. These substances have betaine structures and are distinguished by their ease of preparation and high stabilities [5]. To evaluate the ability of tetrazolium betaines (TB) of this type to undergo reduction, we investigated the polarographic behavior of two series of TB with various substituents attached to the $C_{(5)}$ (I-VIII) and $N_{(3)}$ (IX-XIX) atoms (Table 1).



I-XIX

The polarographic study of the TB was carried out on a dropping mercury electrode with anhydrous dimethylformamide (DMF) in a 0.1 M tetraethylammonium perchlorate base electrolyte at 0 to −2.5 V.† The reduction of most of the TB proceeds in three steps, and the limiting current at concentrations ranging from $4 \cdot 10^{-4}$ to $15 \cdot 10^{-4}$ M is proportional to the depolarizer concentration. In the case of I it was established by millicoulometry that the first two waves are two-electron waves and that approximately four electrons are consumed in the third step. All of the waves have irreversible character according to the results of analysis in $E = f \log [i/(i_{lim} - i)]$ coordinates. The slopes of the waves range from 66 to 150 mV (Table 1); these values considerably exceed the theoretical value for reversible waves (29.5 mV for two-electron waves). However, the dependence of $E_{1/2}$ on the drop period (τ) provides evidence for irreversibility: $E_{1/2}$ is shifted 30-80 mV to the negative region when τ decreases from 2 to 0.3. When proton donors (3.5%) are added to the solution undergoing polarography, the reduction is hindered somewhat in the first step, the second wave remains almost unchanged, and reduction in the third step is facilitated considerably (by 100-300 mV) (Table 2).

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*See [1] for communication XVI.

†All of the potentials are presented relative to the mercury pool.

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TABLE 1. Parameters of the Polarographic Waves of the Reduction of Tetrazolium Betaines (I-XIX) in Anhydrous Dimethylformamide in a 0.1 M $(C_2H_5)_4NClO_4$ Base Electrolyte ($c_{dep} = 4.08\cdot10^{-4}$ M, 70-cm high mercury column)

Compound	R	X	$-E_{1/2}$, V	i_{lim}, μA	Slope of the wave, mV
1	2	3	4	5	6
I	C_6H_5	H	0,35 0,91 1,88	0,72 0,88 1,52	66 71 150
II	CH_3	H	0,49 0,89 1,88	0,92 0,80 1,13	81 61 66
III	n-C_3H_7	H	0,46 1,00 1,87	1,13 0,88 1,14	96 50 60
IV	i-C_3H_7	H	0,40 0,91 1,83	1,13 0,92 1,20	90 55 76
V	$-CH=CH-C_6H_5$	H	0,38 0,86 1,01 1,92 2,32	0,48 0,40 0,28 0,62 1,26	75 65 55 150 150
VI	3-$NO_2C_6H_4$	H	0,33 0,81 1,26 1,81	0,48 0,90 0,44 1,46	80 84 64 95
VII	4-$NO_2C_6H_4$	H	0,33 0,83 1,39 1,77	0,40 0,78 0,44 1,16	100 100 80 88
VIII	$3,4$-$(OCH_3)_2C_6H_3$	H	0,37 0,96 1,71 1,95	0,70 1,10 1,02 0,34	99 120 93 80
IX	C_6H_5	o-Cl	0,35 0,89 1,82	0,40 0,52 0,68	115 71 100
X	C_6H_5	p-Cl	0,39 0,90 1,82	0,44 0,53 0,72	125 66 116
XI	C_6H_5	o-I	0,38 1,01 1,94	0,80 0,65 2,10	92 70 110
XII	C_6H_5	p-I	0,32 1,04 1,91	0,76 0,68 1,90	88 66 120
XIII	C_6H_5	o-Br	0,36 1,04 1,84	0,78 0,62 1,80	85 78 110
XIV	C_6H_5	p-Br	0,41 0,93 1,85	0,70 0,70 1,80	90 80 132
XV	C_6H_5	p-NO_2	0,32 0,82 1,47 1,99	1,10 0,26 0,94 2.00	120 70 70 95
XVI	C_6H_5	o-CH_3	0,40 0,97 1,81 2,42	0,38 0,42 0,36 0,78	66 33 100 100
XVII	C_6H_5	p-CH_3	0,40 0,99 1,79 2,48	0,46 0,46 0,72 0,42	75 88 80 80
XVIII	C_6H_5	p-OCH_3	0,63 1,35	0,46 0,88	150 350
XIX	C_6H_5	p-$N(CH_3)_2$	0,57 1,13 1,95	0,78 0,32 1,72	66 75 110

TABLE 2. Polarographic Waves of Tetrazolium Betaines in Dimethylformamide Containing 3.5% Water

Compound	$-E_{1/2}$, V	i_{lim}, μA	Compound	$-E_{1/2}$, V	i_{lim}, μA
I	0,39	0,60	VII	0,45	0,46
	0,88	0,66		0,90	0,66
	1,16	0,18		1,48	2,50
	1,58	1,20	IX	0,38	0,44
III	0,50	1,05		0,85	0,50
	0,96	0,90		1,59	0,70
	1,62	1,76	XI	0,42	0,80
V	0,49	0,40		1,08	0,65
	0,86	0,60		1,72	2,00
	1,05	0,14	XVIII	0,66	0,42
	1,65	0,28		1,23	0,80
	2,13	1,66			

TABLE 3. Experimental Energies of Activation (Q) in the Polarographic Reduction of Tetrazolium Betaines

Compound	Wave	Q, kJ	Compound	Wave	Q, kJ
I	1	5,77	IX	1	8,42
	2	5,77		2	7,40
		0,00*		3	12,56
	3	7,70	XI	1	12,10
III	1	11,30		2	4,11
	2	7,70			0,00*
	3	2,51		3	6,15
		0,00*			0,00*

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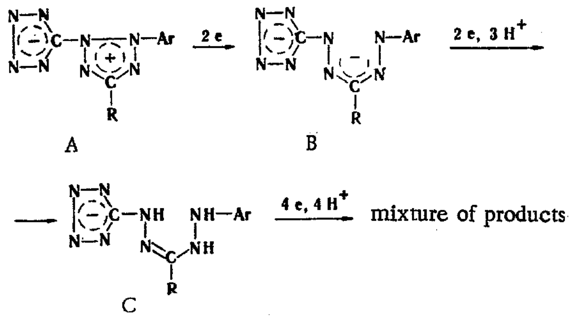
*This is the Q value at temperatures above 40°C.

With allowance for the data on the electrochemical reduction in a series of triaryl-containing tetrazolium salts [6], the reduction of the TB can be represented by the following scheme:



Reduction to give a formazan dianion (B) occurs in the first step without participation of protons. It has previously been shown [7] that tetrazolylformazans can exist in dianionic forms of this type because of the clearly expressed electron-acceptor character of tetrazole. As in the case of triaryltetrazolium salts, the subsequent reduction with the consumption of hydrogen ions evidently proceeds with the formation of a hydrazide derivative (C), after which one observes four-electron reduction (saturation of the C=N bond and cleavage of any N-N bond) with prior protonation, as evidenced by the effect of the addition of water. However, in the case of some of the compounds (II-IV) the reduction ends with one of these steps (judging from the magnitude of the limiting current, a two-electron process occurs here).

The ESR spectra recorded under polarography conditions for I, II, and XIX show weak multicomponent signals of secondary radicals of unestablished structure.

The graphs of the log $i_{lim} = f(1/T)$ dependence for the investigated compounds are straight lines (sometimes with breaks), and the energies of activation calculated from these data (Table 3) lie in the ranges characteristic for diffusion currents and waves complicated by adsorption phenomena [8]. As the temperature rises, one observes a shift in the $E_{1/2}$ values to negative potentials, especially for the second and third waves (up to 2.2 mV/deg); this constitutes evidence for the surface character of the depolarization process [8].

A comparative analysis of the $E_{1/2}$ values of the first waves of TB with different structures shows that electron-donor substituents hinder the reduction. Thus replacement of the phenyl group in the 5 position by an alkyl group (II-IV) promotes a considerable decrease in the electrophilicity of the tetrazolium ring. The introduction of donor substituents in the phenyl ring, particularly a phenyl ring connected to the $N_{(3)}$ atom, has a similar effect. Acceptor substituents in the phenyl ring primarily facilitate the reduction. In the case of halo derivatives the halo substituents have competitive —I and +M effects [9]. Thus the certain degree of hindrance of the reduction of X and XIV may be associated with the strong (and major in this case) +M effect of the p-Cl and p-Br substituents. However, in the case of betaine XII the —I effect of the iodine atom prevails over its weak +M effect (the reduction takes place at less negative potentials). In compounds that contain a nitro group, the behavior of the latter is extremely peculiar. If one judges from the ratio of the heights of the first and second waves, in the case of VI and VII the nitro group is reduced after the tetrazolium ring takes on electrons in the range of quite negative potentials (about —0.8 V). However, when the nitro group is in the phenyl ring attached to the $N_{(3)}$ atom (XV), it undergoes reduction simultaneously with the reduction of the tetrazolium fragment at —0.32 V. Whereas the character of the reduction of the nitro group in the first case recalls the reduction of the nitro group in nitrophenols at high pH values of the solution, in the second case the reduction is definitely similar to the reduction of p-dinitrobenzene in alkaline media [10].

It is important to note that the effects of the various substituents on the reduction of the TB differ from the effects in series of aryl-containing tetrazolium salts, the reduction of which is facilitated by both acceptor and donor substituents [11].

EXPERIMENTAL

The preparation of the investigated compounds and their physicochemical characteristics were described in [1, 5, 7]. The polarographic study was carried out with a Metrohm Polarecord E-261 polarograph at 22 ± 0.5°C in DMF purified by the method in [12] in a 0.1 M tetraethylammonium perchlorate base electrolyte. A mercury electrode with forced drop detachment ($m = 1.13$ mg/sec and $\tau - 0.5$ sec at a mercury column height of 70 cm) was used as the cathode. The pool of mercury served as the anode. The depolarizer concentration was $4.08 \cdot 10^{-4}$ M. Hydrogen was bubbled through the solutions for 20 min prior to the measurements.

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