POLAROGRAPHIC OXIDATION OF ARYL- AND HETARYLFORMAZANS

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The anodic polarographic oxidation of aryl- and hetarylformazans in an aprotic medium was investigated. It is shown that this process has two-electron character for arylformazans and one-electron character for hetarylformazans. It was established that the ability to undergo oxidation decreases in the order 2-benzimidazolyl- > 2-benzothiazolyl- > 2-pyrimidinyl- > 2-quinazolinylformazans.

It is known [1, 2] that formazans are readily oxidized to tetrazolium salts by means of mercuric oxide, lead tetraacetate, isoamyl nitrite, bromine, and bromoimines of acids such as succinic and phthalic acids, as well as by electrochemical methods [3, 4]. The conditions for carrying out the oxidation of hetaryl- and arylformazans differ: The instability of the former in acidic [5] and oxidative [6] media requires carrying out this process in neutral media with a mildly acting oxidizing agent. At the same time, the oxidation of arylformazans in order to obtain tetrazolium salts can be carried out in acidic [5] and oxidative [6] media requires carrying out this process in neutral media with a mildly acting oxidizing agent. At the same time, the oxidation of arylformazans in order to obtain tetrazolium salts can be carried out in acidic media.

No information regarding the electrochemical oxidation of hetarylformazans is available, and even less study has been devoted to this process in the case of arylformazans [3, 4], and it therefore seems of interest to make a comparative study of the effect of the substituents attached to the N_1 and N_5 atoms of the formazyl system on the character of the oxidation of these compounds and on their capacity for electron transfer.

A study of the electrochemical oxidation process in a series of hetarylformazans that contain benzimidazole, benzothiazole, pyrimidine, and quinazoline residues showed that the oxidation of these formazans takes place in two steps (Table 1), whereas the oxidation of their aryl analogs takes place in one step (Table 2). The limiting currents of the anodic process for I-XVII (Table 1) are half the values for XVIII-XXIX (Table 2).

The polarographic waves of all of the investigated formazans I-XXIX have diffusion character [7].

During treatment of the polarographic curves by means of the Nernst equation [7] it was observed that the experimental polarograms for both the aryl- and hetarylformazans are not described by this equation. The irreversible character of the anodic oxidation of arylformazans is also confirmed by cyclical voltammetry and is evidently due to deprotonation, which follows rapid electron transfer [8].

To determine the number of electrons that participate in electrochemical oxidation we used the simultaneous solution of the equation of the limiting current for a rotating disk and the equation of the diffusion process on a stationary electrode [9]. The magnitude of the charge transferred in the case of anodic oxidation of triphenylformazan in an aprotic medium found by this method was found to be 2.2.

An analysis of the two-step polarographic waves of the hetarylformazans and the corresponding cyclical volt—ampere curves makes it possible to propose the formation of intermediate products of one-electron transfer during anodic oxidation. The final products of the electrochemical oxidation of aryl- and hetarylformazans are tetrazolium salts, the formation of which was proved by means of preparative electrolysis.

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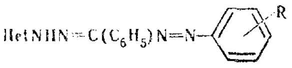
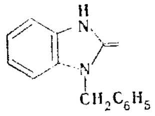
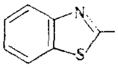
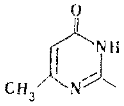
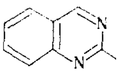
TABLE 1. Anodic Oxidation Potentials of Hetarylformazans



Compound	R	Het	$E'_{1/2}$, V	i'_d, μA	$E''_{1/2}$, V	i''_d, μA
I	H		0,31	—	0,93	—
II	p-NO_2		0,40	—	1,04	—
III	H		0,63	25,0	1,38	22,0
IV	p-OCH_3		0,54	24,0	0,98	21,0
V	o-OCH_3		0,59	25,0	1,03	22,5
VI	p-CH_3		0,49	23,0	1,05	21,0
VII	o-CH_3		0,54	25,0	1,32	21,5
VIII	p-Cl		0,63	24,0	1,41	20,0
IX	p-$COOCH_3$		0,70	23,0	1,44	21,5
X	p-NO_2		0,76	23,0	1,44	21,0
XI	o-NO_2		0,73	24,0	1,46	21,5
XII	H		0,69	21,0	1,60	21,0
XIII	p-OCH_3		0,66	22,5	1,34	22,0
XIV	p-NO_2		0,74	23,0	1,63	20,0
XV	H		0,86	—	1,64	—
XVI	p-CH_3		0,80	—	1,50	—
XVII	p-NO_2		0,94	—	1,65	—

In comparing the oxidation potentials of aryl- and hetarylformazans (Tables 1 and 2) it may be noted that electron-acceptor substituents in both the para and ortho positions of the phenyl rings give rise to an increase in the oxidation potentials, whereas electron-donor substituents decrease them relative to the unsubstituted compounds. As a result of a comparison of the oxidation potentials of the hetarylformazans it is apparent that the ability to undergo oxidation decreases in the order 2-benzimidazolyl- > 2-benzothiazolyl- > 2-pyrimidinyl- > 2-quinazolinylformazans. The change in the oxidation potentials of the formazyl system observed in the series of hetarylformazans under the influence of heterocyclic residues is in good agreement with the change in the energy of the highest occupied orbital of these compunds [10].

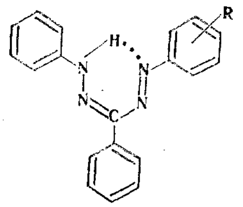
The data from polarographic oxidation are in agreement with the results of chemical oxidation. Benzimidazolylformazans, which contain a π-surplus heteroring, are readily oxidized. Diazinylformazans, which contain π-deficient heterocyclic residues, viz., pyrimidine and quinazoline, are oxidized with greater difficulty.

EXPERIMENTAL

The anodic polarographic oxidation of the formazans was carried out on a platinum rotating disk electrode. The study was made by means of a three-electrode scheme with a P-5827M potentiostat over the range from +0.5 to +2.0 V. An Ag/Ag^+ system in acetonitrile was used as the reference electrode. The depolarizer concentration in anhydrous acetonitrile was $1\cdot10^{-3}$ mole/liter, while the inert electrolyte ($LiClO_4$) concentration was $1\cdot10^{-1}$ mole/liter.

The investigated formazans (I-XXIX) were synthesized by diazo coupling of the arenediazonium salts with the corresponding benzaldehyde aryl(hetaryl)hydrazones. Compounds XVIII-XXIX were described in [1], information regarding formazans I-III was presented in [11], information regarding VI, VII, X, and XI was presented in [12], information regarding XII-XIV was presented in [13], and information regarding XV-XVII was presented in [5]; IV, VIII, and IX were obtained for the first time.

TABLE 2. Anodic Oxidation Potentials of Arylformazans



Compound	R	$E_{1/2}$, V	i_d, μA
XVIII	H	0,65	50,0
XIX	p-OCH_3	0,55	52,0
XX	o-OCH_3	0,64	53,0
XXI	p-CH_3	0,62	51,5
XXII	o-CH_3	0,66	52,0
XXIII	p-OH	0,49	—
XXIV	o-OH	0,54	50,0
XXV	p-Cl	0,67	51,0
XXVI	p-COOH	0,74	46,0
XXVII	o-COOH	0,74	47,0
XXVIII	p-NO_2	0,82	51,0
XXIX	o-NO_2	0,90	50,0

TABLE 3. Characteristics of the Benzothiazolylformazans

Compound	mp, °C	R_f*	Found, %			Empirical formula	Calc., %		
			C	H	N(S)		C	H	N(S)
IV	173	0,61	64,8	4,3	18,1	$C_{21}H_{17}N_5SO$	65,1	4,4	18,1
VIII	215	0,55	61,2	3,6	(8,0)	$C_{20}H_{14}ClN_5S$	61,5	3,5	(8,3)
IX	180	0,68	63,5	4,2	(7,7)	$C_{22}H_{17}N_5SO_2$	63,6	4,1	(7,7)

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*On Silufol plates in an alcohol—chloroform system (1:1).

5-(2-Benzothiazolyl)-3-phenyl-1-(p-chlorophenyl)formazan (VIII). A solution of a diazonium compound from 1.8 g (01013 mole) of p-chloroaniline was added to a cooled solution of 3 g (0.012 mole) of benzaldehyde 2-benzothiazolylhydrazone in 200 ml of ethanol, and the reaction mixture was maintained at pH ∿8 and 0-5°C for 2 h, after which it was neutralized, and the resulting precipitate was removed by filtration, washed with water, and dried to give a product with mp 215°C in 85% yield.

Formazans IV and IX were similarly obtained. Their characteristics are presented in Table 3.

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