RESEARCH ON AROMATIC HETEROCYCLES

XX.* COMPARISON OF THE ELECTROCHEMICAL BEHAVIOR OF NAPHTH-1,2,5-OXADIAZOLES AND THEIR N-OXIDES AND 4,5-DIHYDRO DERIVATIVES IN APROTIC MEDIA

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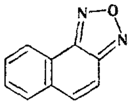
Naphthofurazan is reduced in three stages. The anion radical formed in the first one-electron step is recorded by its ESR spectrum. The absence of a one-electron step in the reduction of naphthofuroxan and dihydro derivatives of sulfonaphthofurazan and sulfonaphthofuroxan should be associated with weakening of the aromatic properties of their molecules.

One-electron transfer may be the determining step in many organic reactions. The immediate transfer of several electrons in one act is less likely than a number of successive one-electron transfers [2]. The elucidation of the capacity of organic molecules participating in reactions for capture of one or several electrons is of great significance. Moreover, polarography may prove to be extremely useful in those cases in which one must isolate the individual steps of electron transfer. Multielectron reduction should proceed in several steps. However, the appearance of a one-electron wave arising as a result of the transfer of one electron to form an anion radical can be recorded only in aprotic solvents.

In the case of aromatic and heterocyclic molecules, including 1,2,5-oxadiazoles, stable radicals that are characterized by the fact that the unpaired electron is a portion of the π-electron cloud distributed along the entire aromatic molecule [3] are formed during one-electron transfer.

In the present research we investigated the electrochemical reduction of naphth-1,2,5-oxadiazole (naphthofurazan) (I), its N-oxide (II) (naphthofuroxan), and the dihydro derivatives of naphthofurazan (III), naphthofuroxan (IV), 8-hydroxynaphthofuroxan (V), and 7-hydroxynaphthoquinone dioxime (VI).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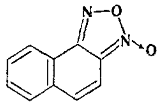
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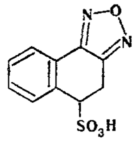
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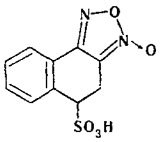
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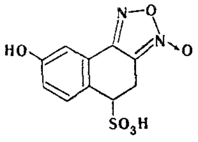
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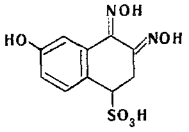
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*See [1] for communication XIX.

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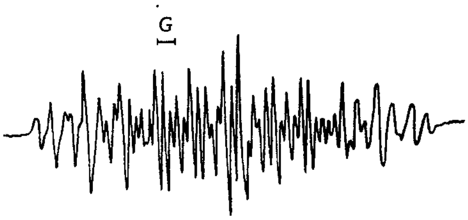


Fig. 1. ESR spectrum obtained during the electrolysis of naphthofurazans in dimethylformamide.

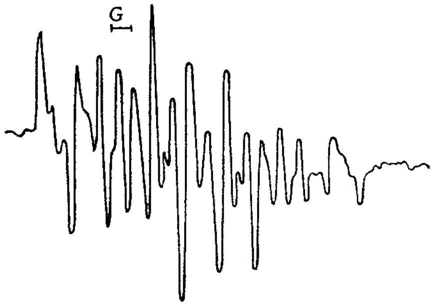


Fig. 2. ESR spectrum obtained during the electrolysis of naphthofurazan-5-sulfonic acid in acetonitrile.

TABLE 1. Polarographic Characteristics of Naphthofurazan

Wave No.	$\varphi_{1/2}$, V	A*	n'†
I	−1,43	1,89	1,3
II	−1,82	3,78	2,6
III	−2,14	2,99	2,1

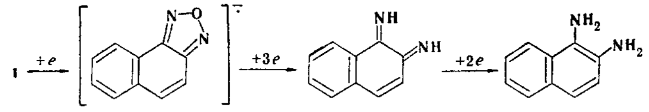
*This is the value of the current relative to the depolarizer concentration.

†This is the number of electrons, transferred, which is determined from the slope and the height of the corresponding waves.

In the case of reduction of naphthofurazan in dimethylformamide (DMF) ($c = 2 \cdot 10^{-4}$ M, with 0.1 M tetraethylammonium iodide as the base electrolyte), three waves, each of which corresponds to transfer of approximately one, three, and two electrons, are seen on the polarogram (Table 1).

An anion radical is apparently formed in the first wave; another three electrons are transferred in the second wave, and a diimine similar to benzofurazan [4] is formed. Two electrons are transferred in the third wave.

Protonation processes are extremely hampered in DMF and may proceed only to a small extent – to the extent that submillimolar amounts of water are present or partial detachment of a proton from the solvent or base electrolyte molecules is possible.



This is possible when active anions or negatively charged products of the electrochemical reaction are formed. When one is examining steps II and III of the indicated mechanism, one must therefore bear in mind that the products of these steps are written only in the customary form (NH). In actuality, these substances exist primarily as the corresponding "aprotic equivalents."

The electrochemical reduction of naphthofurazan in DMF [with a $(C_2H_5)_4N\ ClO^{4-}$ base electrolyte] at a potential of −1.4–1.6 V, i.e., before the beginning of the second wave, leads to the formation of paramagnetic particles. The ESR spectrum of the naphthofurazan anion radical contains nine lines of the hyperfine interaction of the unpaired electron with the nitrogen nuclei (Fig. 1). The spectrum was obtained with higher resolution than in [5]. The nonequivalence of the nitrogen atoms is revealed in this case. It can be assumed that the α- and β- nitrogen atoms have different affinities for an electron. However, calculation of the constants of the hyperfine interaction on these nitrogen atoms shows that the difference is not particularly great and is expressed by 0.5 G ($a_{N_1} = 5.2$ G, $a_{N_2} = 5.7$ G). The hfs of the spectrum also contains splittings from six nonequivalent protons united in two different groups; this is apparently determined by their orientation on the α- or β-carbon atoms of the naphthalene ring ($a_{H_1} = 1.1$ G, $a_{H_2} = 2.5$ G).

The introduction of a sulfo group complicates the spectrum even more (Fig. 2) (by emphasizing the nonequivalence of the atoms) and reduces its extent (there are fewer unsubstituted hydrogen atoms in the naphthalene ring).

The splitting of the wave observed during the reduction of naphthofurazan in anhydrous DMF is apparently explained by the impossibility of protonation of the intermediately formed anion radical; this difficulty vanishes in aqueous solutions [6]. Thus it turns out that, just as in the case of nitro compounds and quinones [7], protonation of the intermediates plays a substantial role in the mechanism of the reduction of 1,2,5-oxadiazoles.

TABLE 2. Polarographic Characteristics of Naphthofuroxan

Working solution	$\varphi_{1/2}$, V	A	n
DMF	−0,38	2,92	2,0
0,1 N $(C_2H_5)_4N^+I^-$	−1,38	8,60	6,0
80% DMF +20% H_2O	−0,11		
0,1 N $(C_2H_5)_4N^+I^-$	−0,39	1,79	1,9
	−0,96	5,62	6,1
Universal buffer	−0,15	1,60	1,47
pH 8.80	−0,56	6,00	5,57

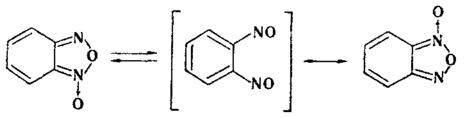
TABLE 3. Polarographic Characteristics of Dihydrosulfo Derivatives

Compound	c, mM	$\varphi_{1/2}$, V	A
III	1,01	−1,95	4,2
IV	0,79	−1,45; −2,10	2,8; 7,04
V	0,79	—1,46; —2,06	1,1; 7,0
VI	0,76	—2,03	7,0

The development of a one-electron wave is not observed in the reduction of naphthofuroxan under the same conditions (in anhydrous DMF); the polarograms are congruent with those obtained in weakly alkaline aqueous alcohol solutions [two waves with n ≃ 2 and n ≃ 6 (Table 2)].

The absence of a one-electron step apparently should be associated with weakening of the aromatic character of the molecule on passing from furazans to furoxans.

A comparison of the polarographic behavior of furoxans, which are the N-oxides of furazans, with other heterocyclic N-oxides shows the difference in the mechanisms of their reduction. Heterocyclic N-oxides are reduced in accordance with a general rule: the exocyclic oxygen is always initially split out to give a two-electron wave, which corresponds to reduction of the N → O group [8, 9]. In contrast, the reduction of furoxans commences with cleavage of the oxadiazole ring [6, 10]. It has been shown [11, 12] that transition between structures Ia and Ib through the intermediate formation of o-dinitroso compound Ic occurs in furoxans.



Ia Ic Ib

The low energy barrier to transition of one of these structures to the other provides a possibility for assuming weakening of the N ··· O bond in the ring. This in all likelihood is the chief reason for the cleavage of the oxadiazole ring that is observed during the reduction of furoxans. Rearrangement of the Ia ⇌ Ib type proceeds readily in aromatic furoxans, while the analogous isomerization of aliphatic furoxans is much more difficult [13]. This means that the intermediate dinitroso derivative for the aliphatic furoxan is substantially less stable than the corresponding intermediates of naphthofuroxan and benzofuroxan. An evaluation of the electrochemical behavior of dihydro derivatives of naphthofuroxan showed that they are close to the aromatic analogs but not to the aliphatic analogs.

The reduction of dihydronaphthofurazan III proceeds in one step in DMF and in aqueous alcohol. As in the case of naphthofurazan, splitting of the wave is not observed. This apparently also can be explained by the decrease in the stability of the product of one-electron reduction as a consequence of disruption of the aromatic character of the naphthofurazan molecule during hydrogenation of the C_4—C_5 bond.

Dihydronaphthofuroxan IV is reduced in the same way as naphthofuroxan in DMF. Two waves with approximately the same height ratio are observed on the polarogram.

It is seen from a comparison of the polarograms of dihydro derivatives of 8-hydroxynaphthofuroxan (V) and 7-hydroxynaphthoquinone dioxime (VI) and from a comparison of the numerical $\varphi_{1/2}$ values (Table 3) that a small additional wave at a more positive potential than the principal wave is observed in the case of hydroxynaphthofuroxan. The closeness of the $\varphi_{1/2}$ values (except for the first wave of dihydronaphthofuroxan) of these compounds makes it possible to assume that the reduction of the sulfo derivative of naphthofuroxan V proceeds through the intermediate formation of dioxime VI, just as in the case of the reduction of naphthofuroxan in aqueous alcohol [6].

EXPERIMENTAL

The polarization curves were recorded with PÉ-312 and LP-60 electronic polarograms. Capillaries with the following characteristics were used: m = 2.11 mg/sec, t = 2.9 sec, h_{Hg} = 400 mm, and m = 1.43

mg/sec; $t = 3.07$ sec, and $h_{Hg} = 400$ mm. Anhydrous DMF, purified by the method in [14], was used as the solvent. A 0.1 M solution of tetraethylammonium iodide was used as the base electrolyte.

A diffusion coefficient (D) of $\simeq 8 \cdot 10^{-6}$ $cm^2 \cdot sec^{-1}$, in analogy with the coefficient determined for naphthalene derivatives from polarographic data [15], was adopted for calculation of the number of electrons (n) from the Il'kovich equation $i_d = 607\ nD^{1/2}cm^{2/3}t^{1/6}$. The diffusion character of the waves follows from the linear dependence of the wave height on the depolarizer concentration.

An electrolytic bridge with a stopcock, half of which was filled with a saturated solution of $(C_2H_5)_4N^+I^-$ in DMF, the other half of which was filled with a saturated aqueous KCl solution, was used to measure the potential of the dropping electrode.

Recrystallized (from alcohol) 1,2-naphthofurazan [16] (mp 79-79.5°), 1,2-naphthofuroxan [17] (mp 124-125°), dihydro derivatives of sulfo-1,2-naphthofurazan [18], sulfo-1,2-naphthofuroxan [19], sulfo-8-hydroxynaphthofuroxan, and sulfo-7-hydroxynaphthoquinone dioxime [20] were used in this study.

The ESR spectra were measured with a Varian-E12 spectrometer. The preparation of the anion radicals was accomplished by an electrochemical method in a glass ampule with an outer diameter of 0.4 cm and a length of 15 cm. Platinum electrodes were soldered to the bottom of the ampule and at a point 10 cm above the bottom of the ampule. Contact with the solution was realized through a mercury drop coating the lower electrode (cathode) and through a platinum lead connected to the upper electrode (anode). Dimethylformamide was used as the solvent, and tetraethylammonium perchlorate served as the base electrolyte.

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