MECHANISM OF THE ELECTROCHEMICAL REDUCTION OF 2-HALO-5-NITROTHIOPHENES IN DIMETHYLFORMAMIDE

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The reduction of 2-bromo-5-nitrothiophene and 2-iodo-5-nitrothiophene in dimethylformamide (DMF) was studied by means of classical and commutated polarography, EPR spectroscopy, a rotating platinum disk electrode with a ring, and preparative electrolysis. It was established that, depending on the nature of the halogen, their anion radicals may undergo further reduction to 2-nitrothiophene anion radicals or decomposition with splitting out of a halide anion and conversion to nitrothienyl radicals, which were identified on the ring electrode. The latter are capable of undergoing dimerization to 2,2'-dinitro-5,5'-dithienyl. The spectra of the anion radicals of 2-nitrothiophene and 2,2'-dinitro-5,5'-dithienyl were recorded by means of EPR. A mechanism for the reduction of halonitrothiophenes is proposed.

The principal products in the electrochemical reduction of p-halonitrobenzenes [1] and 2-halo-5-nitrofurans [2] in aprotic solvents are nitrobenzene and 2-nitrofuran, respectively. However, very little study has been devoted to the mechanism of the electrochemical behavior of 2-halo-5-nitrothiophenes. Only data on the formation of stable anion radicals of 2-chloro-5-nitrothiophene after transfer of the first electron are known [3].

The aim of the present research was to study the peculiarities of the electrochemical reduction of 2-halo-5-nitrothiophenes in dimethylformamide (DMF), since, in our opinion, replacement of the oxygen atom by sulfur in the heteroaromatic ring may lead to a change in the character of the indicated process.

A study of the polarographic behavior of 2-bromo-5-nitrothiophene (I) on a dropping mercury electrode in DMF with a Kalousek commutator [4] showed that it is reduced with reversible transfer of the first electron (Table 1), which leads to anion radicals II. This is followed by a second two-electron wave, which most likely corresponds to the formation and one-electron reduction of 2-nitrothiophene (III), as observed for p-halonitrobenzenes [1]. The third wave corresponds to reduction of the nitro group [5].

2-Iodo-5-nitrothiophene (IV) is reduced with the irreversible addition of two electrons (Table 1). By virtue of the fact that its anion radicals (V) are unstable (τ = 0.11 sec), after transfer of the first electron, they undergo virtually complete decomposition during the lifetime of a drop, and the second electron is consumed in reduction of the products of this decomposition. In addition, a second reversible one-electron wave, which, with respect

TABLE 1. Results Obtained in the Polarographic Reduction of Halonitrothiophenes and Model Compounds in DMF with a Kalousek Commutator

Compound	$-E'_{1/2}$, V	$\Delta E'$, mV	i'_{lim}, μA	τ', sec	$-E''_{1/2}$, V	$\Delta E''$, mV	i''_{lim}, μA	τ'', sec	$-E'''_{1/2}$, V	$\Delta E'''$, mV	i'''_{lim}, μA
I	0,88	60	1,6	0,78	2,04	110	3,1	—	2,32	100	4,8
IV	0,74	95	3,1	0,11	1,03	60	1,6	>5	2,18	110	4,7
III	1,02	60	1,6	>5	2,19	100	4,8	—	—	—	—
IX	0,59	60	1,5	>5	0,74	65	1,5	1,9	—	—	—

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TABLE 2. Splitting Constants in the EPR Spectra of the Anion Radicals Obtained in the Electrochemical Reduction of Halonitrothiophenes and Model Compounds in DMF

Compound	$-E_g$, V	Splitting constants, Oe			
		a_2^H	a_3^H	a_4^H	a_N
I	0,86	—	0,6[a]	1,1[a]	1,7[a]
	2,00	4,8	1,2	5,8	9,5
IV	0,72	—	—	—	—
	1,02	4,8	1,2	5,8	9,5
III	1,02	4,8	1,2	5,8	9,5
IX	0,57	—	0,6[a]	1,1[a]	1,7[a]

[a] Triplets from two equivalent protons in the case of a_3^H and a_4^H ($a_3^{H'}$ and $a_4^{H'}$); a quintet from two equivalent nitrogen nuclei in the case of a_N ($a_{N'}$).

TABLE 3. Results of Electrochemical Reduction of Halonitrothiophenes and Nitrothiophene on a Rotating Platinum Disk Electrode with a Ring in DMF

Compound	Type of electrode	E_{const}, V	$E'_{1/2}$, V	$\Delta E'$, mV	i'_{lim}, μA	Q', %	$E''_{1/2}$, V	$\Delta E''$, mV	i''_{lim}, μA	Q'', %
I	D[a]	—	−0,86	60	19,7	—	−1,03	60	3,5	—
	R[b]	$E^R = -0,72$	−0,86	60	1,23	77	−1,04	60	0,35	21
	R[c]	$E^D = -0,98$	+0,19	60	0,10	—	+0,81	80	0,32	—
IV	D[a]	—	−0,76	70	26,5	—	−1,03	60	10,2	—
	R[b]	$E^R = -0,60$	−0,75	60	0,55	34	−1,02	60	1,0	63
	R[c]	$E^D = -0,90$	+0,19	60	0,18	—	+0,48	70	0,9	—
III	D[a]	—	−1,03	60	16,1	—	—	—	—	—
	R[b]	$E^R = -0,90$	−1,02	60	1,60	99	—	—	—	—

[a] Volt-amperogram on a disk electrode. [b] Volt-amperogram on a ring electrode with a constant ring potential (E_{const}^R) — the potential of the disk electrode is increased. [c] Volt-amperogram on a ring electrode with a constant disk potential (E_{const}^D) — the potential of the ring electrode is increased.

to its potential, coincides with the first reduction wave of nitrothiophene III, is observed on the polarogram. As in the case of thiophene I, the third wave corresponds to reduction of the nitro group and will not be examined subsequently.

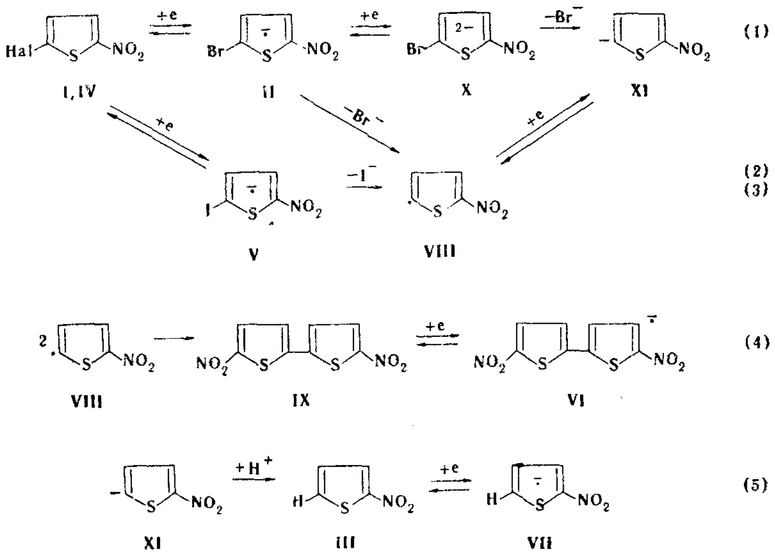
The electrochemical reduction of bromo- and iodonitrothiophenes in a cell with a mercury cathode placed in the resonator of an EPR spectrometer did not make it possible to record the spectra of their anion radicals (II and V). Instead, we observed spectra of anion radicals (VI and VII) of 2,2'-dinitro-5,5'-dithienyl and nitrothiophene, respectively, depending on the cathode potential (Table 2).

To further ascertain the details of the mechanism of splitting out of halogen we studied the behavior of halonitrothiophenes I and IV on a rotating platinum disk with a ring [6]. It should be noted that the range of cathode potentials on platinum is somewhat narrower than on mercury [7], and the waves beyond −1.9 V therefore could not be observed. It is apparent from Table 3 that anion radicals II and V undergo partial decomposition (see Q) during the time that they reside on the disk and are ultimately converted to nitrothiophene III. The latter undergoes further one-electron reduction to anion radical VII. The limiting currents of reduction on the disk therefore correspond to a fraction of the electrons transferred (compared with i'_{lim} of nitrothiophene in Table 3).

Recording of the volt-amperograms of polarization of the ring electrode at a constant disk potential (E_{const}^{D}), which corresponds to the start of the plateau of the limiting current of the first wave on the disk, showed that two waves are observed in the positive potential region. The first (cathode) wave (Table 3) is probably affiliated with reduction of nitrothienyl radical VIII, while the second is affiliated with oxidation of halide anions [8]. Estimates of the half-conversion times of anion radicals II and V by the method in [9] give τ_{II} = 0.14 sec and τ_{V} = 0.02 sec, which differ markedly from the values obtained in the case of reduction on mercury (Table 1). This may be associated with the fact that anion radicals II and V or nitrothienyl radical VIII react with the mercury cathode [10].

Preparative electrical reduction of thiophenes I and IV in an electrolyzer with a platinum cathode with subsequent analysis of the final products showed that, as in the case of bromo- and iodonitrothiophenes, a mixture of dinitrodithienyl IX and nitrothiophene III is formed; the ratios are 1:5 for thiophene I and 2:5 for IV.

The data obtained do not contradict the following scheme for the reduction of halonitrothiophenes:



The first step in the electrochemical reduction of the investigated halonitrothiophenes I and IV is reversible electron transfer, which leads to anion radicals (II and V) of these compounds. The more stable bromonitrothiophene anion radicals II (τ = 0.78 sec) have time under the conditions of polarographic reduction on a dropping mercury electrode with a short dropping period (t = 0.4 sec) [3] to add another electron [p-halonitrobenzenes [2] and 2-chloro(bromo)-5-nitrofurans [3]] and are converted to dianions X. The latter decomposes rapidly with splitting out of a bromide anion (1). The resulting nitrothienyl anions XI split out a proton from the solvent and are converted to nitrothiophene III, which undergoes further one-electron reduction (5) to anion radicals VII. Since the potential of the second wave of bromonitrothiophene III is much more negative than the first reduction potential of III, this wave upon the whole has two-electron character (Table 1).

Anion radicals V, also as a function of the experimental conditions (platinum or stationary mercury electrodes), and anion radicals II are capable of undergoing decomposition via scheme 2 or 3 with the formation of nitrothienyl radicals VII. In this case radicals VIII can ultimately be converted (1, 2, 1, 5 or 1, 3, 1, 5) to nitrothiophene anion radicals VII or to dinitrothienyl anion radicals VI (4), which are recorded by means of EPR spectroscopy.

The difference in the polarographic behavior of thiophenes I and IV is associated with the fact that the second wave for I corresponds to reduction of anion radicals II to dianions X and of nitrothiophene III to anion radical VII, whereas for IV it has reversible one-electron character and corresponds to reduction only of III to VII.

It should be noted that we were able to record the EPR spectra of anion radicals of 2,2'-dinitro-5,5'-dithienyl — the dimer formed in the electrochemical reduction of halonitrothiophenes for the first time, whereas it has not yet been possible to detect products of dimerization of nitrofuryl [3] or nitrophenyl [2, 11] radicals under similar conditions.

The existence of nitrothienyl radicals is also confirmed by data obtained by means of a rotating disk electrode with a ring (Table 3).

In our opinion, the differences in the electrochemical reduction of the indicated compounds are associated with the higher stability of the nitrothienyl radicals as compared with nitrofuryl and nitrophenyl radicals and the higher acceptor capacity of the latter [12].

EXPERIMENTAL

Pure-grade DMF was distilled immediately prior to preparation of the solutions with a column filled with NaA molecular sieves as described in [13]. The base electrolyte was a 0.1 N solution of tetrabutylammonium perchlorate, and the reference electrode was a saturated aqueous calomel electrode.

The construction and characteristics of the rotating disk electrode with a ring were described in [14], while the construction and characteristics of the dropping mercury electrode were described in [3]. The concentration of the starting compounds in the polarographic measurements was $1 \cdot 10^{-3}$ mole/liter. The half-decomposition time (τ) of the anion radicals was determined by means of a Kalousek commutator [4] (Table 1). In the experiments with a rotating disk electrode with a ring [6] the concentration of the investigated compounds was $5 \cdot 10^{-4}$ mole/liter, and the half-decomposition times ($\tau_{II}$and τ_V) of the anion radicals were calculated from the formula presented in [9]. The coefficient (Q) of the yield with respect to current of the anion radicals on the ring was determined from the coefficient of efficiency of the electrode [14].

The methods of recording and calculation of the EPR spectra were described in [3].

Preparative electrical reduction was carried out in an electrolyzer with a platinum cathode [15]. The cathode potential, which was equal to the potential of the start of the plateau of the limiting current of the first wave, was maintained by means of a P-5827M potentiostat. The initial concentration of the compounds was $5 \cdot 10^{-3}$ mole/liter, and the base electrolyte was a 0.3 N solution of tetrabutylammonium perchlorate. After exhaustive electrolysis, some of the solution (∿2 ml) was removed by means of a special device and transferred in an inert atmosphere in a polarographic cell containing a 0.1 N solution of tetrabutylammonium perchlorate in DMF. The ratio of dinitrodithienyl and nitrothiophene was determined from the ratio of the limiting currents (i_{lim}) of the first polarographic waves of these compounds (Table 1).

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