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MECHANISM OF HALOGEN SUBSTITUTION
 IN THE ELECTROCHEMICAL REDUCTION
 OF HALONITROFURANS IN DIMETHYLFORMAMIDE

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The polarographic reduction of 2-halo-5-nitrofurans in dimethylformamide, which leads ultimately to replacement of the halogen by hydrogen to give a nitrofurane, was studied. The ESR spectra of halonitrofurane anion radicals (Hal = Cl, Br) were recorded. Only the spectrum of the nitrofurane anion radical can be observed in the reduction of 2-I-5-nitrofurane. It is shown that the stabilities of the anion radicals of the halonitrofurans and the mechanism of their subsequent transformations depend to a considerable degree on the nature of the halogen.

The halogen in 2-halo-5-nitrofurans (HNF) is relatively easily exchanged by various nucleophilic groups [1, 2], but the mechanism of these transformations has not yet been adequately ascertained. It is known that activated nucleophilic substitution reactions include acts involving electron transfer and the formation of anion radicals (AR) or dianions (DA) as intermediates [3, 4]. It therefore seemed of interest to follow the transformations of the HNF after electron transfer and to study the reactivities of their AR.

We investigated the polarographic behavior of HNF on a dropping mercury electrode (DME) in dimethylformamide (DMF) (Table 1). It is shown that 2-Cl-5-nitrofurane (CNF) adds the first electron reversibility to

TABLE 1. Reduction Potentials of HNF on a DME in DMF in a 0.1 N Bu₄NClO₄ Base Electrolyte (relative to a saturated calomel electrode)

Substituent	$-E'_{1/2}$, V	$\Delta E'$, mV	i'_{lim} , μA	$-E''_{1/2}$, V	$\Delta E''$, mV	i''_{lim} , μA	$-E'''_{1/2}$, V	$\Delta E'''$, mV	i'''_{lim} , μA
Cl ⁻	0,995	58	1,6	2,290	140	7,8	—	—	—
Br ⁻	0,965	59	1,6	2,220	195	7,9	—	—	—
I ⁻	0,840	60	3,1	1,080	59	1,5	2,320	120	4,5
H ⁻	1,060	59	1,6	2,330	120	4,6	—	—	—

*The potentials are given with allowance for the resistance of the cell.

† $\Delta E = E_{3/4} - E_{1/4}$.

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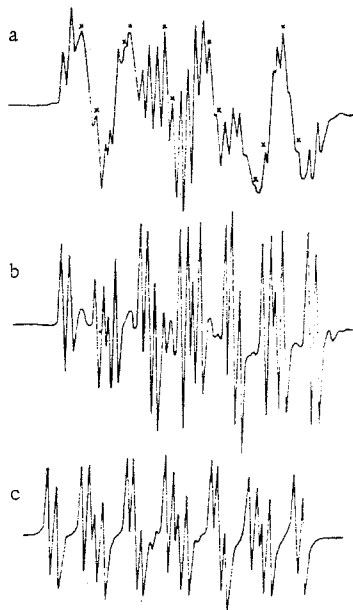


Fig. 1

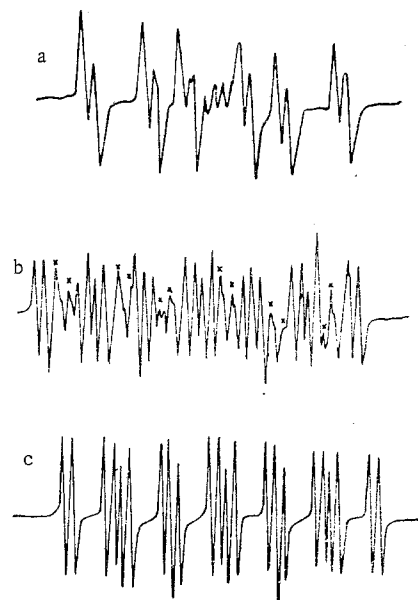


Fig. 2

Fig. 1. ESR spectra of AR obtained electrochemically in DMF: a) AR of CNF (at the potential of the first wave); b) sum of the AR of CNF and the AR of NF (x denotes the lines pertaining to the AR of CNF); c) AR of NF.

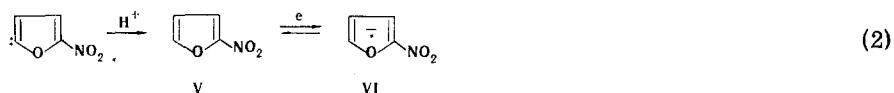
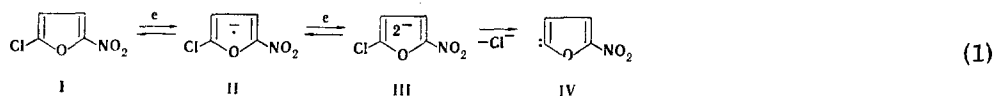
Fig. 2. ESR spectra of the AR obtained electrochemically in DMF: a) sum of the AR of BNF and the AR of NF (at the potential of the first wave) (x denotes the lines pertaining to the AR of BNF); b) AR of NF (at the potential of the second wave of BNF); c) AR of NF (at the potential of the first wave of INF).

TABLE 2. Splitting Constants in the ESR Spectra of the AR of HNF (Oe)

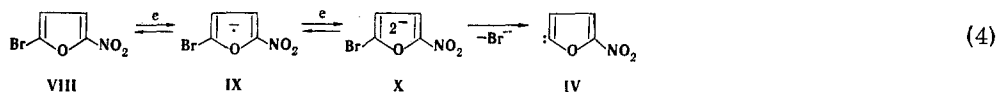
Substituent	a_3	a_4	a_5
Cl ⁻	1,2	6,0	9,7
Br ⁻	0,8	5,6	9,7

give rather stable AR, which are recorded by means of ESR (Fig. 1a). The experimental ESR spectrum of the AR corresponds to the theoretical spectrum (if one disregards the group of lines of low intensity in the center of the spectrum, which appear during generation simultaneously with the principal spectrum and apparently belong to an impurity in the CNF). The second polarographic wave corresponds to an irreversible electrochemical process including the overall transfer of five electrons. Recording of the commutator polarograms with a Kalousek switch demonstrated that one of the steps is reversible. Moreover, reduction of CNF in the resonator of the ESR spectrometer at the potential of the second half-wave leads to the appearance of a complex signal. Construction of the theoretical spectra showed that it is the superimposition of the spectra of the AR of CNF (II) and the AR of NF (VI) (Fig. 1b). The spectrum of the AR of NF [5] is presented in Fig. 1c for comparison. The data obtained make it possible to assume that, like p-nitrochlorobenzene [6], CNF (I) is reduced via schemes (1)-(3).

The dianion (DA) of CNF (III), which decomposes to give Cl⁻ and a carbanion (IV), is formed as a result of the successive transfer of two electrons. Carbanion IV, by splitting out a proton from the solvent is converted to NF (V) and subsequently and reversibly to the AR of NF (VI). We did not study the step involving reduction to a furylhydroxylamine (VII) [7], and it will not be examined subsequently.



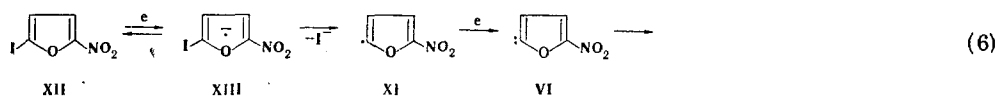
Measurements made with a Kalousek switch at various frequencies showed that, in contrast to the AR of CNF, the AR of 2-Br-5-nitrofuran (BNF) is much less stable, and the first one-electron wave is reversible only at frequencies above 10 Hz. The reduction of BNF (VIII) at the potential of the plateau of the current of the first wave leads to the appearance of a complex ESR signal, and it was found that the intensity of the lines labeled with x's (Fig. 2a) decreases with time. Construction of the theoretical spectra made it possible to isolate the spectrum of the AR of DNF and calculate the splitting constants (Table 2). The second wave has the same character as in the case of CNF (Table 1). When the potential is increased during electrochemical generation to the value corresponding to the start of this wave, the lines pertaining to the AR of BNF (Fig. 1a) gradually decrease in intensity, and the ESR spectrum of the AR of NF (Fig. 2b) is finally observed. It may be assumed that the reduction of BNF proceeds via scheme (4)-(5):



and subsequently via scheme (2).

The IX AR can be reduced to the X dianion, which is subsequently converted to carbanion IV, or, because of its instability, it can decompose to give radical XI and Br^- [scheme (5)]. Since the reduction potential of radical XI is considerably more positive than the potential of the first wave of the BNF, NF will form immediately in this case [schemes (5), (2)]; the appearance of a mixed ESR spectrum is evidently associated with this fact (Fig. 2a).

2-I-5-Nitrofuran (XII) (INF) is reduced with irreversible transfer immediately of two electrons; immediately after this, a reversible one-electron wave evidently corresponding to the reduction of NF to AR (VI) (Table 1) is observed on the polarograms. The small difference in the potentials is, in all likelihood, associated with the inheritance effect [8]. Only the spectrum of the AR of NF can be recorded during electrolysis in the resonator of the ESR spectrometer (Fig. 2c):



and subsequently via scheme (2).

Transfer of the first electron to INF (XII) leads to the formation of an extremely unstable AR (XIII), which decomposes to give I^- and radical XI; the latter adds another electron [scheme (6)], as a result of which the first two-electron wave has irreversible character. The lifetime of the AR of INF is considerably less than $1 \cdot 10^{-3}$ sec, and the character of the first wave therefore does not change at 8-50°C.

Thus, the studies showed that HNF are reduced in DMF to give NF. The stability of the AR of the HNF depends to a considerable degree on the nature of the halogen, and this is evidently associated with the strength of the C-Hal bond in the AR rather than with the distribution of the unpaired electron (Table 2). In conformity with this, the reaction mechanism also changes: in the case of INF the halogen is split out after transfer of one electron, in the case of CNF the halogen is split out after the transfer of two electrons, and in the case of BNF reduction proceeds via a mixed mechanism.

EXPERIMENTAL

Pure-grade DMF was distilled immediately prior to preparation of the solutions by the method in [9]. The HNF were obtained by the methods in [1, 2]. The polarograms were recorded with an LP-7 polarograph at 25°C and 8–50°C. The dropping mercury electrode with a spatula [10] had the following characteristics at -1.0 V: $\tau = 0.4$ s, $m = 1.68$ mg/s. The concentration of the compounds was $1 \cdot 10^{-3}$ mole. The reversibility of the waves and the lifetime of the AR were determined by means of a Kalousek switch at 10–200 Hz. The number of electrons was determined in comparison with the current of the first wave of NF.

The ESR spectra were recorded with a Rubin radiospectrometer at room temperature. The AR were electrochemically generated by the method in [11] in DMF in a 0.1 N Bu_4NClO_4 base electrolyte; the concentration of the compounds was $5 \cdot 10^{-3}$ mole. The ESR spectra were analyzed by the method in [12, 13].

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