FORMATION OF 2,2'-DINITRO-5,5'-DIFURYL ANION RADICALS IN THE ELECTROCHEMICAL REDUCTION OF 2-Br(I)-5-NITROFURANS IN DIMETHYLFORMAMIDE (DMF)

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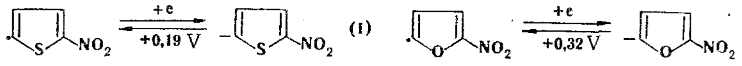
We have recently established [1] that 2,2'-dinitro-5,5'-dithienyl anion radicals are also formed along with nitrothiophene anion radicals in the electrochemical reduction of 2-Br(I)-5-nitrothiophenes, whereas previously [2] in a study of the electrochemical behavior of 2-Br- and 2-I-5-nitrofurans (I, II) we were unable to establish the formation of 2,2'-dinitro-5,5'-difuryl radicals (III). The reason for this, in our opinion, may be the differences in the redox potentials of the pairs (here and subsequently, relative to an aqueous saturated calomel electrode):



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The $E_{1/2}$ value for pair (2) was determined in the present research in DMF by the method used for pair (1) [1]. In comparing the potentials of redox pairs (1) and (2) with the potential for the discharge of mercury in DMF (+0.36 V) it may be concluded that radicals VI are more effective oxidizing agents of the mercury cathode than radicals IV. In fact, when the mercury cathode in the cell for the EPR studies is replaced by a platinum cathode, well-resolved EPR spectra of III anion radicals ($a_{3,3'}{}^{H} = 0.2$, $a_{4,4'}{}^{H} = 0.8$, and $a_{N,N'}{}^{H} = 1.7$ Oe [3]) were obtained in the reduction of furans I and II in DMF. Preparative electrolysis of I and II in an electrolyzer with a platinum cathode showed that the final products of the reduction of I are nitrofuran VIII (7%) and anion radicals III (90%); in the case of II the yield of furan VIII was 28%, while the yield of radicals III was 70%. The experimental method is described in [1, 2].

Thus for the first time we have been able to detect 2,2'-dinitro-5,5'-difuryl radicals (III) in the electrochemical reduction of 2-Br(I)-5-nitrofuran in DMF; this confirms the qualitative analogy between this process and nucleophilic substitution of halogen [3, 4].

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