

ELECTROCHEMICAL MODELING OF THE DEHYDROGENATION  
OF HETEROCYCLES. OXIDATION OF 3,4-DIHYDRO-2-QUINOXALINONE  
DERIVATIVES

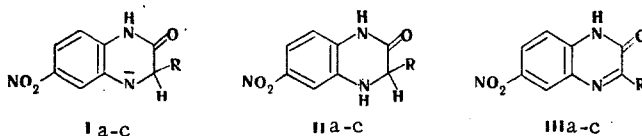
I. M. Sosonkin, G. N. Strogov,  
V. N. Charushin, and O. N. Chupakhin

UDC 547.863.13.16:542.943

A study of the electrochemical oxidation of 3,4-dihydro-2-quinoxalinone derivatives on a rotating platinum disk electrode with a ring showed that their reduction includes the successive detachment of two electrons and two protons.

The dihydro compounds that are formed in the reactions of  $\pi$ -deficient aromatic compounds with nucleophiles have different stabilities. In the case of oxidation under the influence of the starting  $\pi$  acceptors or specially added oxidizing agent they are converted to stable products of nucleophilic substitution of hydrogen [1]. The half-wave potentials of the electrochemical oxidation of the dihydro compounds may serve as a quantitative measure of this process that characterizes the tendency of these compounds to undergo oxidation. The application of electrochemical modeling [2] has also made it possible to ascertain the peculiarities of dehydrogenation as a function of structural factors and the acid-base properties of the solvent. Thus it was recently shown that the electrochemical oxidation of the  $\sigma$  complexes formed by *m*-dinitrobenzene with acetone proceeds via the successive detachment of an electron, a proton, and an electron (EPE) [3]. Depending on their structures, as well as on the properties of the medium, dihydroacridine derivatives are oxidized in turn via EPE [4], EEP [5], or PEE [6] schemes.

It has been reported [7, 8] that the activated nitro group of 2-quinoxalinone, as in the case of aromatic polynitro compounds [9], reacts readily in the presence of diethylamine with aliphatic ketones. However, instead of anionic  $\sigma$  complexes I, uncharged and extremely stable addition products II are formed in this case. The final products (III) of substitution of hydrogen are not formed under the reaction conditions. In order to quantitatively evaluate the resistance of dihydro compounds II to oxidation and to ascertain the peculiarities of their dehydrogenation, in the present research we investigated the principles of the electrochemical oxidation of IIa-c.



I-III a R=2-oxocyclohexyl; b R=CH(COCH<sub>3</sub>)COOC<sub>2</sub>H<sub>5</sub>; c R=CH<sub>2</sub>COCH<sub>3</sub>

The oxidation of dihydro compounds IIa-c on a rotating platinum disk electrode with a ring [10] showed that all of them are oxidized with the irreversible transfer of two electrons (Table 1). In contrast to the previously investigated dihydro compounds [3, 5], cation radicals IV are much less stable (Table 1), as evidenced by the low coefficients of the yields with respect to the current on the ring ( $E_{\text{const}}^{\text{r}}$  corresponds to the foot of the wave for oxidation on a disk) and the rate constants for monomolecular decomposition of the cation radicals estimated by the method in [11]. A cathode wave of reduction of two protons is observed in the case of scanning of the potential of the ring electrode at a constant disk potential ( $E_{\text{const}}^{\text{d}}$ ) corresponding to the beginning of the plateau of the limiting current in the oxidation of IIa-c [5] (Table 1). It should be noted that the oxidation potentials of dihydro compounds IIa-c are relatively independent of substituent R and have much

All-Union Scientific-Research and Planning Institute of Monomers, Tula 300026. S. M. Kirov Ural Polytechnic Institute, Sverdlovsk 620002. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 2, pp. 261-263, February, 1981. Original article submitted March 27, 1980.

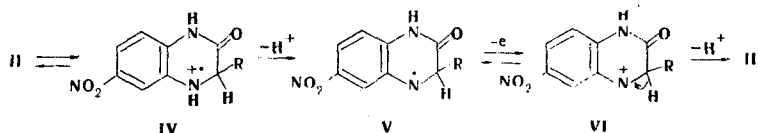
TABLE 1. Results of Electrochemical Oxidation of 3,4-Dihydro-2-quinoxalinone Derivatives (IIa-c) on a Rotating Disk Electrode with a Ring in DMF

Compound	Alkali concn., * mole liter <sup>-1</sup> · 10 <sup>-4</sup>	E <sub>const.</sub> , V	Disk			Ring				
			E <sub>1/2</sub> , V	ΔE, mV	i <sub>lim</sub> , μA	E <sub>1/2</sub> , V	ΔE, mV	i <sub>lim</sub> , μA	Q, %	k, sec <sup>-1</sup>
IIa	0	E <sup>r</sup> = +0.80	+1.00	200	25.0	—	—	<0.002	<0.2	>1000
	0	E <sup>r</sup> = -0.65	+1.00	200	25.0	+1.01	170	2.6	208	
	0	E <sup>d</sup> = +1.20	—	—	—	-0.47	170	2.6	208	
	2.5	—	+0.29	190	3.0	—	—	—	—	
	5.0	—	+1.03	140	23.0	—	—	—	—	
IIb	0	E <sup>r</sup> = +0.80	+1.09	210	28.6	+1.10	80	0.006	0.4	650
	0	E <sup>r</sup> = -0.65	+1.09	210	28.6	+1.12	160	2.7	189	
	0	E <sup>d</sup> = +1.30	—	—	—	-0.47	170	2.7	189	
	2.5	—	+0.37	200	2.6	—	—	—	—	
	5.0	—	+1.10	160	26.0	—	—	—	—	
IIc	0	E <sup>r</sup> = +0.80	+1.02	230	28.0	+1.02	70	0.004	0.3	870
	0	E <sup>r</sup> = -0.65	+1.02	230	28.0	+1.03	170	2.9	204	
	0	E <sup>d</sup> = +1.20	—	—	—	-0.46	160	2.7	193	
	5.0	—	+0.30	200	5.2	—	—	—	—	
	5.0	—	+1.05	200	22.5	—	—	—	—	

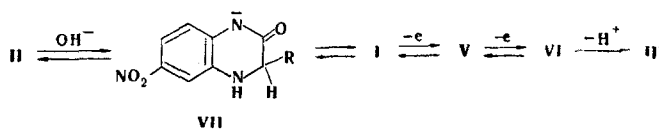
\*Tetrabutylammonium hydroxide was used as the alkali.

more positive values as compared with dihydroacridine derivatives (+0.70 V [4]) as well as with anionic σ complexes (E<sub>1/2</sub> = 0.24-0.6 V [3]).

In analogy with the results obtained in [4, 5], it may be assumed that the first step in the oxidation of dihydro compounds IIa-c is electron transfer leading to cation radicals IV. The decomposition of the latter takes place very rapidly (see the k values in Table 1) and may lead to different radical particles as a function of which a proton of the heteroring is split out in the process. If one takes into account the results of the electrochemical oxidation of dihydropyridines [12, 13], the detachment of a proton from the nitrogen atom with the formation of radicals V seems most likely. As a rule, the radicals are oxidized more readily than the starting compounds [3-6], and they will therefore undergo oxidation to cations VI at the potential of the first wave. The detachment of a proton from cations VI leads to final dehydrogenation products III.



The rate-determining step in dehydrogenation via this scheme is detachment of the first electron or proton. In fact, when alkali is added to the investigated solutions of IIa-c, an intense coloration is observed and, in addition, a new oxidation wave appears in the region of more negative potentials. The limiting current of this wave increases as the amount of added alkali is increased, while the limiting current of the wave of oxidation of uncharged IIa-c undergoes a corresponding decrease so that their sum remains virtually constant (Table 1). It may be assumed that this results in the production of anion VII, which exists in prototropic equilibrium with σ complex I, the oxidation of which proceeds in the same way as the oxidation of anionic σ complexes [3] and also leads to substitution products III.



Thus a study of the electrochemical behavior of the products of addition of ketones to 6-nitro-2-quinoxalinone showed that they are oxidized with the successive detachment of two electrons (E) and two protons (P) and that path EPEP or PEEP is realized, depending on the acid-base properties of the medium.

## EXPERIMENTAL

The method used to record the volt-ampere curves on the rotating disk electrode and its construction, characteristics, and preparation are described in [14]. The number of electrons transferred on the disk electrode was calculated relative to the first one-electron wave of the oxidation of N,N,N',N'-tetramethyl-p-phenylenediamine ( $i_{lim} = 16 \mu A$ ) starting from the assumption that the coefficients of diffusion of the depolarizer are inversely proportional to the square root of the molecular weight. The concentration of the compounds was  $5 \cdot 10^{-4}$  mole/liter. A saturated calomel electrode served as the reference electrode, and the base electrolyte was 0.1 N Bu<sub>4</sub>NClO<sub>4</sub>.

## LITERATURE CITED

1. O. N. Chupakhin and I. Ya. Postovskii, Usp. Khim., 45, 908 (1976).
2. I. M. Sosonkin, A. Ya. Kaminskii, S. S. Gitis, V. A. Subbotin, and T. K. Polynnikova, Zh. Org. Khim., 9, No. 7, 1470 (1973).
3. I. M. Sosonkin, G. N. Strogov, A. Ya. Kaminskii, G. E. Troshin, and F. F. Lakomov, Zh. Org. Khim., 15, 1895 (1979).
4. I. M. Sosonkin, V. A. Subbotin, V. N. Charushin, and O. N. Chupakhin, Dokl. Akad. Nauk SSSR, 229, 888 (1976).
5. I. M. Sosonkin, O. N. Chupakhin, and A. I. Matern, Zh. Org. Khim., 15, 1976 (1979).
6. O. N. Chupakhin, I. M. Sosonkin, A. I. Matern, and G. N. Strogov, Dokl. Akad. Nauk SSSR, 250, 875 (1980).
7. O. N. Chupakhin, V. N. Charushin, and Yu. V. Shnurov, in: News in the Chemistry of Nitrogen-Containing Heterocycles [in Russian], Vol. 1, Zinatne, Riga (1979), p. 166.
8. O. N. Chupakhin, V. N. Charushin, and Yu. V. Shnurov, Zh. Org. Khim., 16, 1064 (1980).
9. S. S. Gitis and A. Ya. Kaminskii, Usp. Khim., 47, 1970 (1978).
10. A. N. Frumkin and L. N. Nekrasov, Dokl. Akad. Nauk SSSR, 126, 115 (1959).
11. W. J. Albery and S. Bruckenstein, Trans. Faraday Soc., 62, 1946 (1966).
12. Ya. P. Stradyn', G. Ya. Dubur, Ya. V. Ogle, and Ya. R. Uldrikis, in: News in the Chemistry of Nitrogen-Containing Heterocycles [in Russian], Vol. 2, Zinatne, Riga (1979), p. 102.
13. Ya. P. Stradyn', Yu. I. Beilis, G. Ya. Dubur, and T. L. Slonskaya, Izv. Akad. Nauk Latv. SSR, No. 3, 372 (1978).
14. I. M. Sosonkin, V. A. Subbotin, and A. V. Fedayainov, Zh. Org. Khim., 15, 344 (1979).