6. Yu. A. Zhdanov, and V. I. Minkin, Correlational Analysis in Organic Chemistry [in Russian], Izd. Rost. Univ., Rostov-on-Don (1966), p. 14
7. G. N. Lipunova, A. P. Zeif, N. P. Bednyagina, and L. N. Shchegoleva, Zh. Org. Khim., No. 8, 1757 (1972).
8. A. I. Kitaigorodskii, P. M. Zorkii, and V. N. Bel'skii, Structure of Organic Substances. Data of Structural Investigations 1929-1970 [in Russian], Nauka, Moscow (1980), pp. 97, 152, 179, 527.
9. P. B. Fisher, B. L. Kaul, and H. Zollinger, Helv. Chim. Acta, 51, 1449 (1968).
10. V. I. Minkin and V. A. Bren', Reactivity of Organic Compounds [in Russian], Vol. 4, Tartu (1967), p. 112.

EPR AND POLAROGRAPHY OF NITROAZOLES.

5.* FIRST STEP IN THE ELECTROCHEMICAL REDUCTION OF 2-SUBSTITUTED 5(6)-NITROBENZIMIDAZOLE USING A ROTATING PLATINUM RING-DISK ELECTRODE

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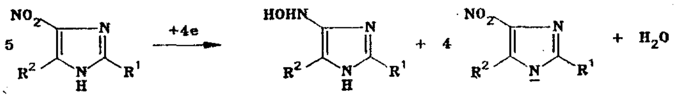
Using a rotating platinum ring-disk electrode, the electrochemical reduction of 2-substituted 5(6)-nitrobenzimidazoles at the platinum disk in acetonitrile and the oxidation of their radical anions at the ring were studied. During the reduction molecular hydrogen forms by a bimolecular reaction of two primary radical anions. The correlating of electrochemical quantities with the σ_I, σ_R, and σ^* substituent constants are evidence that $E^d_{1/2}$ depends on substituent resonance and induction effects to about the same extent, whereas i^d_{lim}, n, and $E^r_{1/2}$ depend predominantly on the resonance effect.

We have previously reported [2-4] on the electrochemical reduction of a number of nitroazole derivatives in acetonitrile. It was presumed that at the potentials of the first wave, nitroazoles not substituted at nitrogen gave unstable radical anions (RA) that decomposed with the elimination of hydrogen. The resulting nitroazole anions were reduced further at second-wave potentials to radical dianions (RDA) that were detected by EPR.

A somewhat different scheme of electrochemical reduction of nitroimidazoles in dimethylformamide was proposed by Kargin and co-workers [5]. In their opinion, only one-fifth of the starting molecule undergoes an electrochemical conversion at the first-wave potentials:

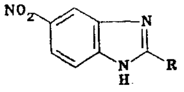


(1)

At second-wave potentials the deprotonated nitroimidazole molecule is reduced to an RDA.

When this scheme is realized, no hydrogen ought to form in the first step of the reaction.

Thus, in order to define more accurately and study in more detail the processes occurring at first-wave potentials, we undertook an electrochemical study of some 2-substituted 5(6)-nitrobenzimidazoles (I-VII) using a rotating platinum ring-disk electrode [6]



I-VII

I $R=N(CH_3)_2$, II $R=OC_2H_5$, III $R=OCH_3$, IV $R=H$, V $R=COOH_3$, VI $R=CF_3$, VII $R=CN$

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*For Communication 4, see [1].

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TABLE 1. Polarographic Study of 2-Substituted 5(6)-Nitrobenzimidazoles

Compound	R	E^r_{const}, V	Disk		n	Range		Q*
			$E_{1/2}{}^d$, V	$i_{lim}{}^d$, μA		$E_{1/2}{}^r$, V	$i_{lim}{}^d$, μA	
I	$N(CH_3)_2$	−0,70	−1,15	30,80	0,94	−0,92	0,12	0,022
II	OC_2H_5	−0,60	−1,12	31,60	0,97	−1,08	0,48	0,084
III	OCH_3	−0,60	−1,11	28,20	0,84	−1,02	0,03	0,006
IV	H	−0,70	−1,14	26,00	0,73	−1,04	0,19	0,041
V	$COCH_3$	−0,55	−0,96	22,00	0,67	−0,89	0,05	0,013
VI	CF_3	−0,60	−0,90	19,20	0,61	—	—	—
VII	CN	−0,40	−0,76	16,60	0,49	−0,77	0,05	0,017

*$Q = i_{lim}{}^r/(i_{lim}{}^d \cdot N_{eff})$ (coefficient of current efficiency).

TABLE 2. Oxidation Parameters of Hydrogen Formed in Decomposition of Radical Anions of 2-Substituted 5(6)-Nitrobenzimidazoles

Compound	R	E^d_{const}, V	$E^{H_2}_{1/2}$, V	$i_r^{H_2}$ μA	Q, %
I	$N(CH_3)_2$	−1,55	+0,07	1,20	26,0
II	OC_2H_5	−1,35	+0,17	1,80	31,0
III	OCH_3	−1,30	+0,20	1,40	27,6
IV	H	−1,30	+0,15	2,20	47,0
V	$COCH_3$	−1,15	+0,17	1,45	26,0
VI	CF_3	−1,00	—	—	—
VII	CN	−1,10	—	—	—
H_2*	—	—	+0,20	11,00	—

*Obtained when hydrogen is blown through.

This method was chosen for two reasons. First, hydrogen is electrochemically active at platinum group metals. Second, the method permits the study of processes occurring directly in solution, and avoids certain phenomena related to the electrical double layer [6].

Table 1 shows the first-wave reduction potentials of compounds I-VII in acetonitrile at the platinum disk and the oxidation potentials of their radical anions at the ring. In successive recordings the voltamperogram shifts toward the negative potentials (without cleaning the electrode). Moreover, the radical anion oxidation wave (except for the voltamperogram of VI) is recorded at the ring electrode; i.e., the transfer of the first electron is reversible. The wave shift may be related to adsorption on platinum of the hydrogen that forms when the radical anion decomposes, and consequently to a change in electrode surface. To identify the hydrogen, voltamperometric curves were recorded at the ring electrode. At the disk electrode a potential was established equal to the plateau of the first-wave limiting current. In most cases (except the voltamperograms of VI and VII) a hydrogen oxidation wave appeared (Table 2). The same potential region shows an intense hydrogen oxidation wave when hydrogen gas is blown through the solution. Some scatter in the values of the hydrogen oxidation-wave potential is due to proton adsorption on the electrode ring, which shifts the wave to the positive region with successive recordings (Fig. 1).

Hydrogen evolution in the decomposition of 2,4-dinitroaniline radical anion was also observed in [7]. There it was shown that hydrogen formation is due to a bimolecular reaction of two radical anions. Indeed the formation of atomic hydrogen, a very powerful reducing agent in the form of kinetically independent particles, is less probable. To verify the validity of such an assumption for the reduction of nitrobenzimidazole derivatives, we studied the dependence of the first-wave limiting current on the square root of the number of rotations at both disk and ring ($i_{lim}\sqrt{m}$). In the latter case, the constant ring potential corresponded to the start of the plateau of the limiting current of hydrogen oxidation (Fig. 2,a). As this figure shows, at the disk electrode all the test compounds show a linear dependence of $i_{lim}{}^d$ on $\sqrt{m}$, which can be evidence that nitrobenzimidazole consumption is a first order reaction. At the same time, at the ring the dependence of $i_{lim}{}^r$ on $\sqrt{m}$ is nonlinear (Fig. 2b), i.e., hydrogen formation is a reaction of higher than first order. Here the rate constant of hydrogen formation lies in the time range of the method that we applied, and is limiting [6].

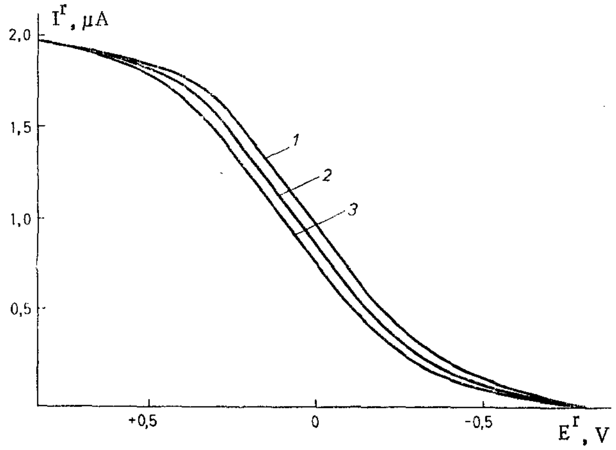


Fig. 1. Hydrogen oxidation wave at the disk for constant potential, is equal to the initial limit reduction flow area of 5(6)-nitrobenzimidazole. 1 — 3: wave interference at final recordings without electrode cleansing.

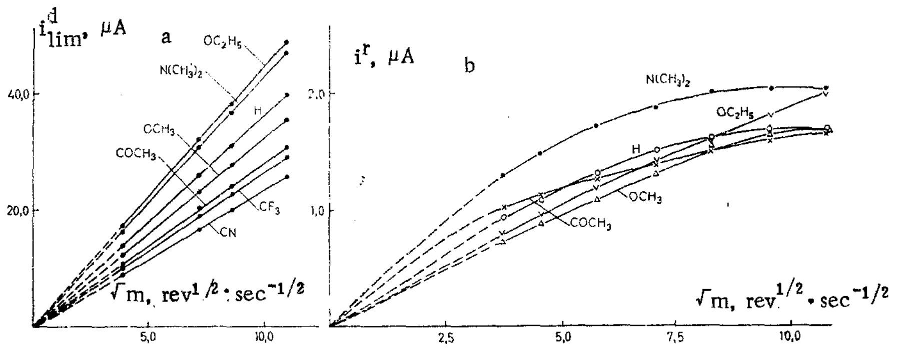
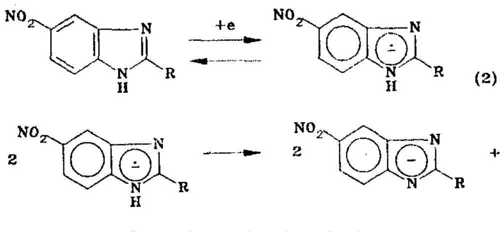


Fig. 2. Dependence on rate of rotation for 2-substituted 5(6)-nitrobenzimidazoles: a) limiting current of first reduction wave at disk electrode; b) limiting current of hydrogen oxidation wave at ring electrode.

On the other hand, if the formation of molecular hydrogen were simply related to $H^{\cdot}$ dimerization (the rate constant is close to the diffusion constant), then the rate-determining step ought to be $H^{\cdot}$ formation, and the relation of i_{lim}^{r} to $\sqrt{m}$ ought to have been linear, because the radical anions decompose by a monomolecular mechanism.

From the data that have been presented we can propose a bimolecular mechanism for hydrogen formation:



(2)

As we have already noted, compounds VI and VII behave somewhat anomalously. Although their dependence of i_{lim}^{d} on $\sqrt{m}$ is linear, the first wave limiting current corresponds to a formal transfer of 0.5-0.6 electron. At the same time, if the starting compounds were dissociating, then proton reduction ought to take place at the platinum. But the wave that belongs to this process is absent.

It should also be noted that the hydrogen current efficiency (Q) for the other compounds (Table 2) is less than 100%. Furthermore for VI and VII the ratios of first-wave and second-wave limiting currents are respectively 0.83 and 0.78; i.e., the hydrogen that is formed and the starting compounds themselves are consumed by some other kind of reactions, such a reduction of the nitro group by adsorbed hydrogen [8, 9].

TABLE 3. Parameters of Correlations* $Y = a\sigma_I + b\sigma_R + d$, and $Y = a\sigma_I + b\sigma_R + c\sigma^{\cdot} + d$, for 2-Substituted 5(6)-Nitrobenzimidazoles.

Y	a	b	c	d	R	S	n	σ_I, %	σ_R, %	$\sigma^{\cdot}$, %
$-E_{1/2}^{d}$	0,53±0,11	0,14±0,05	—	−1,13±1,82	0,957	0,04	7	57±10	43±10	—
	0,43±0,04	0,28±0,03	0,23±0,04	−1,17±0,17	0,992	0,02		28±3	50±4	21±3
i_{lim}^{d}	−12,17±4,51	−9,45±2,10	—	25,93±3,56	0,954	1,61	7	32±9	68±9	—
	−9,32±3,16	−13,18±2,17	−6,43±2,93	26,98±4,15	0,973	1,24		17±5	66±7	17±7
n	−0,27±0,15	−0,32±0,07	—	0,75±1,89	0,943	0,06	7	24±11	76±11	—
	−0,20±0,12	−0,42±0,08	−0,17±0,11	0,78±0,13	0,957	0,05		12±7	72±10	15±9
$-E_{1/2}^{r}$	0,29±0,22	0,08±0,10	—	−1,00±0,20	0,676	0,08	6†	—	—	—
	0,05±0,05	0,33±0,03	0,46±0,05	−1,08±0,19	0,983	0,02		3±3	59±4	38±4

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*R, correlation coefficient; S, standard deviation; n, number of points; σ_I, contribution of inductive component; σ_R, contribution of resonance component; $\sigma^{\cdot}$, contribution of radical-stabilizing factor.

†Data for R = CF_3 point are lacking.

Table 3 shows the correlations of the electrochemical parameters with the substituent constants σ_I and σ_R and the radical-stabilization factor $\sigma^{\cdot}$ [10-12]. The substituent effect on $E_{1/2}^d$ is achieved with equal contributions from inductive and resonance components, as on $E'_{1/2}$ in [1]. It is of interest that the nature of the substituent has a significant effect on i_{lim}^d, predominantly by a resonance mechanism (≈70%).

The relation between i_{lim}^d (and n) and the respective pK_a values [1] is extremely slight for I-VII (r = 0.8-0.9). Indeed, as we have previously shown [1], the substituent effect on the dissociation constant (pK_a) of nitrobenzimidazoles is exerted predominantly by the induction mechanism (≈80%).

EXPERIMENTAL

The nitrobenzimidazoles were prepared by known procedures [1] and were purified by recrystallization and vacuum sublimation immediately before use.

Pure grade acetonitrile was purified by the procedure of [13] immediately before use.

The supporting electrolyte was 0.1 N tetra-n-butylammonium perchlorate. The reference electrode was a saturated calomel electrode.

The procedure for recording voltamperograms at the rotating disk electrode with a ring is described in [14]; the construction of the latter, in [15, 16]. Electrode properties: $r_1 = 1.00$, $r_2 - 1.04$, $r_3 = 1.07$ mm, m = 3,000 rpm, efficiency coefficient N_{eff}, calculated from oxidation of tetramethyl-p-phenylenediamine, 0.18. Number of electrons, n, transferred at disk electrode was calculated under the assumption that the diffusion coefficients of the depolarizes are proportional to the square root of the molecular weight. Concentrations in solution were $5 \cdot 10^{-4}$ M.

Statistical treatment of the polarographic data was carried out by a standard program on a BÉSM-6 computer. The percent contributions of substituent effects were calculated by a program based on the method proposed in [17]. Values of σ_I, and σ_R are taken from [18], $\sigma^{\cdot}$ from [12].

LITERATURE CITED

1. V. A. Lopyrev, L. I. Larina, L. Kh. Baumane, E. F. Shibanova, R. A. Gavar, S. M. Ponomareva, T. I. Vakul'skaya, and Ya. P. Stradyn', Khim. Geterotsikl. Soedin., No. 9, 1246 (1984).
2. V. A. Lopyrev, L. I. Larina, T. N. Rakhmatulina, E. F. Shibanova, T. I. Vakul'skaya, and M. G. Voronkov, Dokl. Akad. Nauk SSSR, 242, 142 (1978).
3. T. I. Vakul'skaya, L. I. Larina, O. B. Nefedova, L. P. Petukhov, M. G. Voronkov, and V. A. Lopyrev, Khim. Geterotsikl. Soedin., No. 10, 1398 (1979).
4. T. I. Takul'skaya, L. I. Larina, O. B. Nefedova, and V. A. Lopyrev, Khim. Geterotsikl. Soedin., No. 4, 523 (1982).
5. Yu. M. Kargin, V. Z. Latypova, A. I. Arkhipov, R. Kh. Fassakhov, T. A. Eneikina, and G. P. Sharnin, Zh. Obshch. Khim., 50, 2582 (1980).
6. L. N. Nekrasov, "Advances in science and technology," Élektrokhimiya, 17, 148 (1981).
7. S. G. Mairanovskii, I. M. Sosonkin, and T. K. Ponomareva, Élektrokhimiya, 14, 567 (1978).
8. F. P. Sargent and E. M. Gardy, Can. J. Chem., 54, 275 (1976).
9. A. V. Bulatov, A. T. Nikitaev, and M. L. Khidekel', Izv. Akad. Nauk SSSR Ser. Khim., No. 4, 924 (1981).
10. T. H. Fisher and A. M. Meierhoefer, J. Org. Chem., 43, 224 (1978).
11. S. Dincturk and R. A. Jackson, J. Chem. Soc. Perkin Trans. 2, No. 8, 1127 (1981).
12. W. J. Leigh, D. R. Arnold, R. W. Humphreys, and P. C. Wong, Can. J. Chem., 58, 2537 (1980).
13. I. M. Sosonkin, A. N. Domarev, É. G. Kaminskaya, A. I. Tolstikov, F. F. Lakomov, and A. Ya. Kaminskii, Zh. Prikl. Khim., 44, 950 (1971).
14. I. M. Sosonkin, V. A. Subbotin, and N. V. Fedyainov, Zh. Org. Khim., 15, 344 (1979).
15. A. N. Domarev, V. I. Kumantsov, and I. M. Sosonkin, Élektrokhimiya, 17, 459 (1981).
16. G. E. Troshin, A. N. Domarev, F. F. Lakomov, V. I. Kumantsov, and I. M. Sosonkin, Élektrokhimiya, 17, 897 (1980).
17. C. G. Swain and E. C. Lupton, J. Am. Chem. Soc., 90, 4328 (1968).
18. S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, in R. W. Taft (editor), Prog. Phys. Org. Chem., Vol. 10, Academic Press, New York (1973), p. 1.