POLAROGRAPHIC STUDY OF AZO DERIVATIVES OF 3-HYDROXYPYRIDINE

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It was established that in most cases azo derivatives of 3-hydroxypyridine are reduced successively in two one-electron steps at more positive potentials than azobenzene on a dropping mercury electrode in anhydrous dimethylformamide (DMF) with a 0.05 N solution of tetraethylammonium perchlorate as the base electrolyte. However, one two-electron wave was observed for some compounds; this is evidently associated with self-protonation owing to the presence of the appropriate substituents. Some 3-hydroxypyridine derivatives exist in DMF in various tautomeric forms, as a result of which additional reduction waves appear. More pronounced reduction with respect to the azo group is observed only for three of the investigated compounds.

Azo dyes with one or several —N=N— groups in their molecules constitute the most extensive class among all organic synthetic dyestuffs. The azo compounds recently obtained on the basis of 3-hydroxypyridine absorb light in the visible region, and it has been suggested that they be used as dyes [1, 2]. Despite its apparent simplicity, the structure of azo dyes has been and, in fact, still is under discussion. A rather large number of studies [3-12] have been devoted to the electrochemical investigation of azo compounds; however, azo derivatives of 3-hydroxypyridine have not been investigated in this respect. The aim of the present research was to study a number of derivatives of 3-hydroxypyridine by means of polarography.

It was recently demonstrated [13] that 6-phenylazo-3-hydroxypyridine derivatives in organic solutions exist in the form of two equilibrium tautomers (azo and hydrazone forms). A peculiarity of these compounds is the ease with which the tautomeric equilibrium is shifted as a function of the nature of the solvent, during which the amount of the azo form ranges from 10 to 90%. On the one hand, since the electronegativity of the nitrogen atom is higher than that of the carbon atom, the transition from azobenzene derivatives to azopyridine derivatives should lead to facilitation of electrical reduction, i.e., to a shift of the half-wave potential ($E_{1/2}$) to the positive region. On the other hand, the introduction of an electron-donor hydroxy group in the pyridine ring should hinder reduction by shifting $E_{1/2}$ to the negative region. However, there are data available that indicate that the OH group has a variable effect on the polarographic behavior of various compounds depending on the proton-donor properties of the medium [14]. It is apparent from Table 1 that a comparison of the half-wave potential of the first wave ($E'_{1/2}$) of azobenzene, which, according to our data, is −1.315 V under similar conditions, with the $E'_{1/2}$ values of VII, XIII, and XVII shows that azo derivatives of 3-hydroxypyridine are reduced more readily than azobenzene. Azo derivatives of 3-hydroxypyridine are reduced on a dropping mercury electrode in anhydrous DMF to give one, two, or three waves (Fig. 1), depending on the presence of various substituents; the heights of the waves indicate different reduction mechanisms for the indicated compounds (Table 1). 3-Hydroxypyridine itself is not reduced under the indicated conditions, which is in complete agreement with the rather high energy of the lower vacant molecular orbital (LVMO) that we calculated for it (E_{LVMO} = 4.5 eV). However, II, which differs from it only with respect to the phenyl substituent in the 2 position of the pyridine ring, forms a wave of unexplained nature at a high negative potential ($E_{1/2}$ = −1.95 V).* It might be assumed that III-V would be reduced via the same

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*Here and everywhere, relative to a saturated colomel electrode (SCE).

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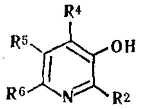
TABLE 1. Polarographic Characteristics of Azo Derivatives of 3-Hydroxypyridine [in anhydrous dimethylformamide with 0.05 N $N(C_2H_5)_4ClO_4$ as the base electrolyte]



Compound	R^2	R^4	R^5	R^6	Half-wave potentials relative to a saturated calomel electrode, V		Current constants^a	
					$-E'_{1/2}$	$-E''_{1/2}$	I_1	I_2
I	H	H	H	H	—	—	—	—
II	C_6H_5	H	H	H	1,950	—	1,015	—
III	C_6H_5	H	H	$N_2C_6H_4OCH_3$-*p*	1,290	1,951	3,16	1,75
IV	C_6H_5	H	H	$N_2C_6H_4SO_3H$-*p*	1,115	2,010	1,97	0,84
V	C_6H_5	H	H	$N_2C_6H_4Br$-*p*	1,175^b	1,547	1,38	1,42
VI	C_6H_4Br-*p*	H	H	$N_2C_6H_5$	1,263	1,973	1,75	1,47
VII	$C_6H_4CH_3$-*p*	H	H	$N_2C_6H_5$	1,233^b	1,612	1,02	0,86
VIII	$C_6H_4OCH_3$-*p*	H	H	$N_2C_6H_5$	1,235	—	2,66	—
IX	$C_6H_3(OCH_3)_2$-2,4	H	H	$N_2C_6H_5$	1,19	1,19	1,79	0,94
X	OCH_3	H	H	$N_2C_6H_5$	0,879	1,251	2,36	0,66
XI	I	H	H	$N_2C_6H_5$	1,42	1,952	5,42	1,75
XII	Cl	H	H	$N_2C_6H_5$	1,313^b	1,54	0,67	1,04
XIII	$CH(CH_3)_2$	H	H	$N_2C_6H_5$	1,245	1,671	1,50	0,99
XIV	$CH_2C_6H_5$	H	H	$N_2C_6H_4Br$-*p*	1,082	—	2,10	—
XV	CH_3	H	H	$N_2C_6H_4SO_3H$-*p*	1,135	1,927	2,29	1,87
XVI	C_6H_5	H	$N_2C_6H_5$	OH	1,45	—	2,22	—
XVII	$N_2C_6H_5$	H	$CH_2C_6H_5$	H	1,265	2,035	1,49	1,12
XVIII	$N_2C_6H_5$	$COOC_2H_5$	H	H	1,412	—	1,361	—
XIX	$N_2C_6H_4Br$-*p*	H	H	COOH	1,056^b	1,50	0,816	1,039
XX	$N_2C_6H_4OCH_3$-*p*	COOH	H	H	1,394^b	—	1,178	—
XXI	$N_2C_6H_4Br$-*p*	COOH	H	H	1,146^b	1,94	0,887	0,543

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[a] $I = \bar{i}/c \cdot m^{2/3} \cdot \tau^{1/6}$, where $\bar{i}$ is expressed in microamperes, m is expressed in milligrams per second, c is expressed in moles per liter, and τ is expressed in seconds. [b] The $E_{1/2}$ and I values of the first additional waves, respectively, for the compounds are: 0.485 V and 0.514 for V, 0.443 V and 0.226 for VII, 0.445 V and 0.645 for XII, −0.310 V and 0.155 for XIX, −0.185 V and 0.324 for XX, −0.159 V and 0.525 for XXI, and −0.385 V and 0.610 for XXIII.

Fig. 1. Polarograms: 1) the base electrolyte – a 0.05 N solution of $N(C_2H_5)_4ClO_4$ in dimethylformamide; 2) XVIII; 3) VI.

mechanism, the only difference being primarily the $E'_{1/2}$ values. In fact, III, which contains an OCH_3 substituent that is conjugated with the reaction center through the phenyl ring and has the least pronounced electron-acceptor properties in the investigated series of substituents, has the most negative $E'_{1/2}$ value. This pattern is, in general, also observed if one disregards the first additional wave of V, which is due in all likelihood to the partially protonated form of this compound. The high current constant (I) for III, which requires further study, must also be noted. Proceeding from our calculations in accordance with the Ilkovic equation (Table 1), which are in good agreement with the liter-

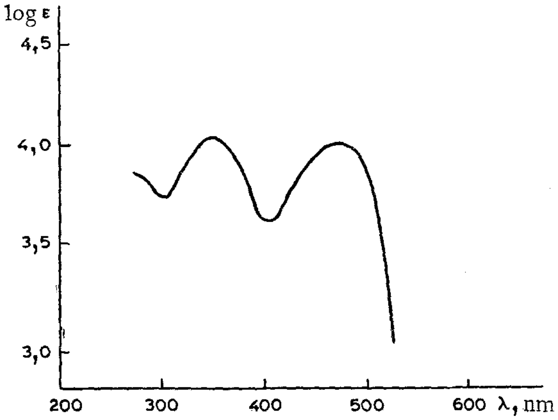

Fig. 2. Electronic absorption spectrum of 2-methoxy-3-hydroxy-6-phenylazopyridine (X) in CCl_4.

ature data [6], for the majority of the compounds of the series that we investigated one can propose a simple reduction mechanism that is characteristic for azo derivatives in an aprotic medium:

$$R'{-}N{=}N{-}R \xrightarrow{+e} R'{-}N{=}N{-}\dot{R}^{-} \xrightarrow{+e} R'{-}N{=}N{-}R^{2-}$$

Thus, as we have already pointed out above, the effect of a heteroring basically reduces to facilitation of the reduction of the azo group. The certain differences in the polarographic characteristics are due, in addition to other reasons, to the different adsorbabilities of the investigated compounds, which may be promoted by the presence of both a pyridine ring and an azo grouping if one takes into account the different stereometries of the molecules as a function of the different substituents [7-9].

The next series of compounds, which can be classified as monotypic compounds that differ only with respect to the different substituents in the phenyl ring in the 2 position of the pyridine ring, is made up of VI-IX (Table 1). It is interesting to follow the effect of halo substituents in different positions in the case of V and VI. The effect of conjugation of the bromine atom through the phenyl ring in V facilitates reduction with respect to the azo group of the molecule, whereas in VI the effect of this substituent in a phenyl ring that is not conjugated with the azo group even hinders reduction somewhat, which is confirmed by the rather negative $E'_{1/2}$ value for VI. The x-ray diffraction data indicating the high degree of coplanarity of hydroxybenzenes and pyridylazonaphthols [15, 16] and the fact that the bathochromic shift of the maximum of the long-wave band of the azo form is symbatic to the electron-donor properties of the substituent are arguments in favor of the possibility of conjugation in the investigated systems. It is apparent from the data in Table 1 that VII and VIII have virtually identical $E'_{1/2}$ values but differ markedly with respect to their reduction mechanisms: VII, which has a CH_3 substituent, is reduced in two one-electron steps via the scheme indicated above (here, just as in the case of V, there is a small forewave, evidently due to the protonated form with a large positive $E_{1/2}$ value), whereas methoxy derivative VIII is reduced in one two-electron step. If one compares the characteristics of III and VIII, which differ with respect to the position of the OCH_3 substituent, one may also observe a difference in their reduction mechanisms. The electron-donor properties of the OCH_3 substituent in III shift its $E'_{1/2}$ value to the negative side, whereas the ability of the OCH_3 group to form a hydrogen bond prevails in the case of VIII. When we compared the polarographic characteristics of VIII and IX, we observed that the introduction of yet another methoxy group in the meta position of the phenyl ring in IX equalizes, as it were, the effect of the OCH_3 group in the para position, and this compound is reduced in two one-electron steps with a less negative $E'_{1/2}$ value. It must be noted that during its electrical reduction, IX forms very elongated (along the axis of potentials) waves (from −0.885 to −1.485 V for the first wave and from −1.735 to −2.235 V for the second wave), i.e., they are irreversible, whereas reversible character of the first reduction wave is indicated for most aromatic azo derivatives [5-11]. The coplanarity of the molecule is evidently markedly disrupted in the case of IX.

The next series of compounds (X-XIII) can also be classified as monotypic compounds with respect to the character of the substituents: They differ only with respect to the simple substituents in the 2 position of the pyridine ring (Table 1). In this series one's attention is directed to the large positive $E'_{1/2}$ and $E''_{1/2}$ values for X, which are characteristic for compounds of the quinone type such as anthraquinone [17]. In fact, the quinonehydrazone structure of 2-methoxy-3-hydroxy-6-phenylazopyridine (X) is confirmed by electronic spectroscopy (Fig. 2) [13]. According to the data from the IR and electronic spectra, a protolytic equilibrium (hydroxyazo $\rightleftharpoons$ quinonehydrazone tautomerism) is characteristic for X. In Fig. 2 the long-wave λ_{max} band at 480 nm is a characteristic of the quinonehydrazone form, while the band with λ_{max} 365 nm is a characteristic of the hydroxyazo form. Large negative $E'_{1/2}$ values are observed for the investigated series in the case of azo derivatives with I and Cl substituents (XI and XII), and this indicates a contribution of primarily the effect of polar conjugation of these substituents with the reaction center [18], which is, of course, much more pronounced than for V with a C_6H_5Br substituent. Compound XI is reduced in the first step, as demonstrated by the magnitude of current constant I_1, with the consumption of more than two electrons. A forewave with a large positive $E_{1/2}$ value is observed in the polarographic reduction of XII. Disregarding X, the most positive $E'_{1/2}$ value in this series is observed for XIII with a $CH(CH_3)_2$ substituent.

Compounds XIV and XV with Br and SO_3H substituents conjugated with the azo group through the phenyl ring are very similar with respect to their polarographic characteristics to the analogous V and IV; the most positive $E'_{1/2}$ values in the entire investigated series of compounds are observed in this case, and this is in complete agreement with the electronic effect of these substituents. The current constants of these compounds are rather high; however, only the first reduction step is observed in the case of bromo derivative XIV.

The dihydroxypyridine with an azo group in the 5 position of the pyridine ring (XVI) is reduced irreversibly on a mercury cathode; this is confirmed by the extremely great elongation of the polarographic wave over a very wide range of potentials, viz., from −0.935 to −1.935 V (arbitrary $E_{1/2} = -1.45$ V). The reduction of XVII, which contains an azo group in the 2 position of the pyridine ring, is somewhat hindered as compared with, for example, VIII and XIII, which, like all of the compounds examined above, contain an azo group in the 6 position. It is reduced in two one-electron steps with negative $E_{1/2}$ values. The introduction of an ester grouping in the 4 position of the pyridine ring hinders the reduction of the azo group to an even greater extent, shifting $E_{1/2}$ to the very negative region (−1.412 V); only one one-electron wave is observed (XVIII). The presence of a carboxy group in the 6 position in XIX, on the other hand, facilitates reduction; this is associated, in our opinion, with self-protonation of this compound, which explains the large positive values of the half-wave potentials. The reduction process in this case is in all likelihood controlled by the rate of protonation, and that is why the current constants have somewhat depressed values [19]. The presence of carboxy groups in the 4 position of the pyridine ring in XX and XXI leads to the appearance of even more positive first waves, and the I values demonstrate that they have kinetic character, which is probably due to self-protonation of the molecules of these compounds.

EXPERIMENTAL

The polarographic measurements were made with a Radelkis OH-102 recording electronic polarograph (Hungary) relative to a saturated calomel electrode (SCE) at 25 ± 0.1°C with respect to a three-electrode system on a dropping mercury electrode with capillary characteristics $m = 2.693$ mg/sec and $\tau = 3.48$ sec (for an open circuit). The potentials were controlled by means of a P-307 high-resistance dc potentiometer. The anhydrous DMF used as the solvent was purified by the method in [20]; the $N(C_2H_5)_4ClO_4$ used as the base electrolyte was prepared from $N(C_2H_5)_4I$ and $Mg(ClO_4)_2$ and was purified by the method in [21]. The electronic absorption spectra were recorded with a Specord UV-vis spectrophotometer. The azo derivatives of 3-hydroxypyridine investigated in this research were synthesized and purified by the methods described in [22].

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