ELECTROCHEMICAL CHARACTERISTICS OF ANTHRAPYRIDONE AND ITS DERIVATIVES

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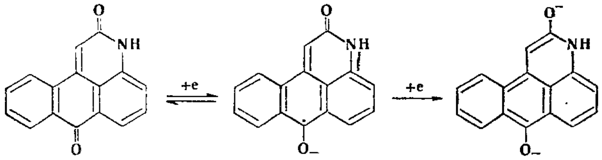
A mechanism is proposed for the electrical reduction of anthrapyridone and its derivatives on a dropping mercury electrode in anhydrous dimethylformamide. Parallelism in the electrochemical behavior, under the indicated conditions, or anthrapyridone and anthraquinone derivatives was noted. A linear correlation of the half-wave potential with the calculated energies of the lower vacant molecular orbital by the Hückel MO LCAO method within the Pariser–Parr–Pople approximation was found. The half-wave potentials correlate satisfactorily with the enthalpies of the intramolecular hydrogen bond of the investigated compounds.

Anthrapyridone (7H-dibenz[f,i,j]isoquinoline]2,7](3H)dione) and its derivatives have not been investigated polarographically. According to quantum-chemical calculations, the anthrapyridone molecule includes a quinoid grouping [1], and this provides a basis for the assumption that it will be readily reduced on a dropping mercury electrode and characterized by a low redox potential. The goal of the present communication was a study of anthrapyridone and its derivatives by polarography.

It has been shown [1, 2] that the electronic structures of the amide and keto groups in anthrapyridone are close to the electronic structures of these groups in anthraquinone and 2-pyridone. Since the acceptor effect of the carbonyl group is evidently greater than that of the condensed pyridone ring, one should have expected that anthrapyridone would be reduced at more negative potentials than anthraquinone. In fact, as seen from the data in Table 1, the half-wave potential of the first wave of anthrapyridone is shifted by 0.16 V to the more negative region than in the case of anthraquinone [3, 4]. At the same time, the half-wave potential of the second wave ($E_{1/2}^{II}$) of anthrapyridone I has a more positive value than in the case of 9,10-anthraquinone (−1.33 and −1.44 V, respectively). The polarographic behavior of anthraquinone and its derivatives is determined to a great degree by the nature of the medium (for example, see [5, 6]) and primarily by its proton-donor capacity. Studies of solutions in dimethylformamide (DMF) and acetonitrile showed [7-9] that in these aprotic solvents anthraquinone and its derivatives are reduced stepwise in two steps. As seen from Table 1, current constants A_1 and A_2 indicate that the mechanism of the electrical reduction of anthrapyridone and its derivatives on a dropping mercury electrode in anhydrous DMF is basically the same as in the case of anthraquinone: two electrons are added successively in two one-electron steps via the following scheme:



However, in the case of 1-hydroxy-N-methylanthrapyridone (V) the reduction mechanism is apparently different. According to our data, V is a strong acid ($pK_a = 6.43$ in 50% ethanol), and it may be assumed that self-protonation occurs in DMF, in agreement with the data in [10]. However, this problem requires additional study. A third wave is observed for a number of compounds [anthrapyridone (I), N-methylanthrapyridone (IV), etc.], and this indicates further reduction of fragments of the molecule and, in the case of 1-nitro-N-methylanthrapyridone (IV), probably reduction of the nitro group. In the case of 6-bromo-N-methylanthrapyridone (XVIII) the halogen is possibly reduced after reduction of the quinone grouping. It is known [8] that in the case of anthraquinone and

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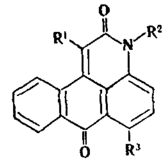
TABLE 1. Polarographic Characteristics of Anthrapyridone Derivatives in Anhydrous Dimethylformamide [0.1 N $N(C_2H_5)_4I$ Base Electrolyte] and Calculated Energies of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Vacant Molecular Orbital (LVMO)



Compound	R¹	R²	R³	Half-wave potentials, V, s.c.e.			Current constants			Hückel MO, −β	
				$-E^{I}_{1/2}$	$-E^{II}_{1/2}$	$-E^{III}_{1/2}$	A^*_1	A^*_2	A^*_3	HOMO	LVMO
I	H	H		0,978	1.328	2,36	2,00	1,42		0.730	0,106
II	OH	H		0,962	1,757		1,26	1,96		0,497	0,202
III	2-Methoxyanthrapyridone			1,017	1,469	2,33	1,89	1.73		0,564	0,186
IV	H	CH_3		0,952	1,338	2,40	2,32	1,51		0,717	0,122
V	OH	CH_3		0.532	1,838		1,62	4,05		0,497	
VI	NO_2	CH_3		0,573	0,758	2,33	2,22	1,62			
VII	CN	CH_3		0,573	1,066		1,67	1,87			
VIII	N-Pyridino	CH_3		0,613	0,916	1,41	1,47	2,06	1,45		
IX	$CH_3CONH—$	CH_3		0,863	1,363		2,03	1,72			
X	Cl	CH_3		0,922	1,248		2,48	2,40		0,686	0,132
XI	CH_3O	CH_3		1,046	1,487		2,80	3.27		0,528	0,181
XII	N-Anilino	CH_3		1,084	1,598		2,11	1,42		0,287	
XIII	N-Piperidino	CH_3		1,128	1,508		2,15	1,42			0,224
XIV	N-Cyclohexylamino	CH_3		1,160	1,558		2,09	1,30		0,313	0,265
XV	$C_6H_{13}NH$	CH_3		1,197	1,567		1,72	1,00			
XVI	NH_2	CH_3		1,245	1,670		1,71	1,80		0,381	0,242
XVII		CH_3	OH	0,872	1.405		1,92	1,60		0,603	0,161
XVIII		CH_3	Br	0,909	1,315	1.977	1,77	1.72	2,07	0,686	0,121
XIX		CH_3	$C_6H_{13}NH—$	1,089	1,429		1,64	1,37		0,339	0,243
XX		CH_3	NH_2	1,167	1,502		1,96	1,67		0,402	0,223

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* $A=\frac{\bar{i}_d}{c \cdot m^{2/3} \cdot \tau^{1/6}}$, where $\overline{i_d}$ is measured in microamperes, m is measured in milligrams per second, c is measured in moles per liter, and τ is measured in seconds. The limiting current of the first and second waves is diffusion controlled.

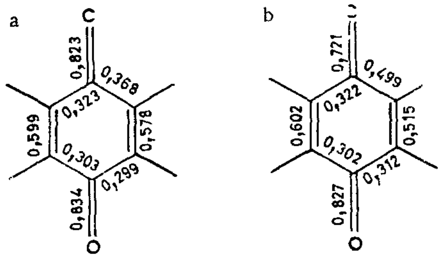

Fig. 1. Bond orders of the quinoid fragments: a) anthrapyridone; b) 2-methoxyanthrapyridone.

its derivatives the limiting current constant of the first wave is larger, on the average, by a factor of 1.25 than the limiting current constant of the second wave. This regularity is also basically observed for anthrapyridone and its derivatives, although deviations are observed in a number of cases.

The close values of the $E_{1/2}$ and A polarographic characteristics (Table 1) of O- and N-methyl isomers III and IV indicate similar mechanisms of the electrical reduction of these compounds. There is no substantial difference between compounds that contain two carbonyl groups or only one.

In fact, according to our calculations by the Pariser–Parr–Pople (PPP) method within the Dewar variant, III and IV have similar quinoid groupings [1, 2] (Fig. 1). In this case the preferred assumption is that the first electron adds to the ketone carbonyl group rather than to the amide group, since the negative charge (−0.406) of

TABLE 2. Shifts of the Frequencies of the Stretching Vibrations of the NH and OH Bonds ($\Delta\nu_{OH}$ and $\Delta\nu_{NH}$ in cm^{-1}) and Changes in the Enthaplies of the Intramolecular Hydrogen Bonds (ΔH_{IHB} in kcal/mole) in Anthrapyridones

Substituent	$\nu^*_{NH...O}$ and $\nu_{OH...O}$	$\Delta\nu_{NH}$	lg ΔH	ΔH°	ΔH_{IHB}
1-NH_2	3428	44	0,15	1,41	1,03
1-NHC_6H_5	3338	134	0,46	2,90	2,12
6-NHC_6H_{13}	3305	167	0,52	3,35	2,45
6-NH_2	3391	81	0.32	2,09	1,53
6-OH	3000	648	0,91	8.08	5,92
1-OH	3264	384	0.76	5,75	4,21

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* Frequencies of the vibrations of free OH and NH groups: $\nu^\circ_{NH} = 3472\ cm^{-1}$, $\nu^\circ_{OH} = 3648\ cm^{-1}$.

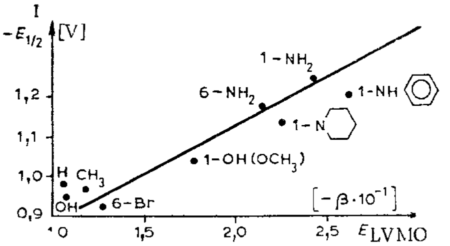

Fig. 2

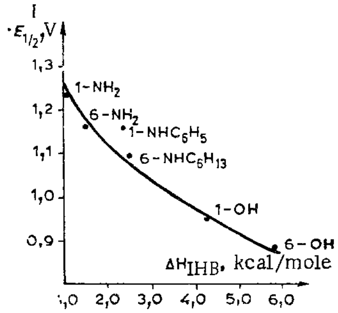

Fig. 3

Fig. 2. Correlation between the $E_{1/2}{}^I$ and E_{LVMO} values of some anthrapyridone derivatives.

Fig. 3. Correlation of the $E_{1/2}{}^I$ half-wave potentials and IHB enthalpies for amino- and hydroxyanthrapyridones.

the former is lower than that of the latter (−0.476). In the case of III the second electron most likely adds to the C=C bond in the para position relative to the C=O group.

The addition of an electron during polarographic reduction of a molecule is usually interpreted as occupation by this electron of the lowest vacant molecular orbital (LVMO) [11]. A linear relationship should exist between the energy of this π orbital and the corresponding $E_{1/2}$ value. As seen from Table 1, the measured $E_{1/2}$ values correlate satisfactorily with the LVMO energies calculated by the Hückel MO method (Fig. 2).

It is apparent from Table 2 and Fig. 3 that in the case of anthrapyridones in which an intramolecular hydrogen bond is formed [12] the $E_{1/2}{}^I$ values lie in the more positive region as compared with the values in the case of compounds that do not form an intramolecular hydrogen bond. For example, on passing from N-methylanthrapyridone (IV) to 6-hydroxy-N-methylanthrapyridone (XVII), the $E_{1/2}{}^I$ value decreases by 0.080 V, and on passing from 1-piperidino-N-methylanthrapyridone (XIII) to 1-hexylamino- (XV) and 1-cyclohexylamino-N-methylanthrapyridone (XIV) it decreases by −0.069 and −0.032 V, respectively.

The enthalpies of the intramolecular hydrogen bonds of the amino- and hydroxyanthrapyridones were determined from the equations proposed by Terent'ev [13]:

$$\lg\Delta H^\circ = A + p\lg\Delta\nu,$$
$$\Delta H_{IHB} = \Delta H^\circ(1-\Delta\Delta H)\alpha = \Delta H^\circ \cdot 0.732,$$

where A = −0.92, p = 0.65, $\Delta\nu$ is the shift in the frequency of the stretching vibrations of the XH groups, $(1-\Delta\Delta H)$ is the correction for the linearity of the XH...O intramolecular hydrogen bond (IHB) in the six-membered ring, and α is the experimental shift of the $\nu_{XH(X=O)}$ band.

Since amino and hydroxy derivatives of anthrapyridone with free NH and OH groups are unknown, to estimate the shift of the frequency of the ν_{NH} and ν_{OH} stretching vibrations of these groups during the formation of an intramolecular hydrogen bond in the investigated compounds we used the free ν_{NH} and ν_{OH} frequencies in the IR spectra of 2-amino- and 2-hydroxyanthraquinones in the gas phase [14] (ν_{NH} 3472 cm^{-1}, and average $\nu^{as}_{NH_2}$, $\nu^{s}_{NH_2}$, and ν_{OH} value 3648 cm^{-1}).

It is apparent from Table 2 and Fig. 3 that there is a satisfactory correlation between the calculated IHB enthalpies (ΔH_{IHB}) and the half-wave potentials ($E_{1/2}^{I}$). The observed relationship between ΔH_{IHB} and $E_{1/2}^{I}$ in anthrapyridones is in agreement with the polarographic data in [15] for anthraquinone and its methoxy and hydroxy derivatives.

EXPERIMENTAL

The polarographic measurements were made with an OH-102 electronic recording polarograph (Hungary). A dropping mercury electrode with the following capillary characteristics was used for the reduction of the investigated compounds: $m = 2.251$ mg/sec, and $\tau = 3.6$ sec. The electrochemical cell was thermostatted at 25 ± 0.1°. The potentials were monitored by means of a P-304 high-resistance dc potentiometer. All of the measurements were made in anhydrous DMF purified by the method in [16] with a 0.1 M $N(C_2H_5)_4I$ base electrolyte (recrystallized from alcohol). Some of the anthrapyridone derivatives were calculated by the Hückel MO LCAO method (Hückel MO) with the aid of the parameters in [17] and by the MO LCAO method within the Pariser–Parr–Pople approximation [18].

Anthrapyridone and its derivatives were obtained and purified as in [12].

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