REACTION CENTER IN THE OXIDATION OF AMINO DERIVATIVES OF 2-PHENYLBENZIMIDAZOLE IN DIMETHYLFORMAMIDE

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The electrochemical oxidation of amino derivatives of 2-phenylbenzimidazole on a rotating platinum disk with a ring in neutral and acidic dimethylformamide was investigated. It is shown that the investigated compounds are oxidized in two electrochemical steps that include reversible one-electron processes, as a consequence of which the potentials have thermodynamic significance and can serve as a measure of the relative reactivities of these compounds in the oxidation reaction. The imidazole ring undergoes oxidation in acidic media ($HClO_4$) because of protonation of the amino groups, whereas the amino group is the reaction center in neutral DMF.

Aromatic amines are oxidized relatively easily by transition metals [1], peroxide compounds [2], and oxygen [3], as well as electrochemically [4], in which case the potentials obtained from the electrochemical data are a relative measure of their oxidation capacities [5]. Amino derivatives of 2-phenylbenzimidazole may have up to three reaction centers capable of undergoing oxidation — the amino groups and the imidazole ring. Depending on the acid–base properties of the medium, one of the centers may undergo protonation, in which case the oxidation mechanism will change [6, 7]. It has been shown [8, 9, 10] that in the case of aqueous solutions of amino derivatives of 2-phenylbenzimidazole the benzimidazole ring has a higher basicity than the amino group, although the basicity of aniline in water ($pK_{BH^+} = 4.58$) [11] is somewhat higher than the basicity of 2-phenylbenzimidazole ($pK_{BH^+} = 4.51$) [12]. Moreover, a change in the nature of the solvent may lead to an appreciable redistribution in the order of the basicities of the investigated compounds [13]. Since information regarding the oxidation of amino derivatives of 2-phenylbenzimidazole in aprotic solvents is evidently unavailable, it seems of interest to follow the effect of the substituent and the properties of the medium on the character of the oxidation of 2-phenylbenzimidazoles in order to ascertain the reaction center that primarily undergoes oxidation.

As seen from Table 1, the character of the waves for the investigated products depends to a significant degree on the position of the substituent: Thus 2-phenylbenzimidazole undergoes oxidation with reversible transfer of one electron, whereas the remaining compounds are oxidized in two one-electron steps. Recording of the voltamperograms with a ring at a potential corresponding to the foot of the first wave (Table 1) showed that both waves have reversible character for II-IV, and a drop in current is not observed after the first wave. The potentials therefore have thermodynamic significance and may serve as a measure of the relative reactivities of the investigated compounds in the oxidation reaction. The incorporation of an amino group in benzimidazole system II leads to a pronounced decrease in the oxidation potential (~1.0 V). At the same time, the phenyl portion of the molecule is much less sensitive to the nature of the substituent (See Table 1, III). It may be assumed that in the case of imidazoles II-IV the first step corresponds to oxidation of the amino group, while the second step involves directly the imidazole ring.

A study of the effect of added perchloric acid on the character of the oxidation of the investigated compounds showed that in the case of 2-phenylbenzimidazole the introduction of $HClO_4$ causes a shift of the potential of the wave to the positive region without an appreciable change in the limiting current. At $HClO_4$ concentrations above $1 \cdot 10^{-3}$ M the wave is

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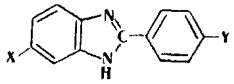
TABLE 1. Results of Electrochemical Oxidation of 2-Phenylbenzimidazole Derivatives on a Rotating Platinum Disk with a Ring in DMF



Compound	Substituents		$HClO_4$*, M	Disk				Ring			
	X	Y		$+E'_{1/2}$, V	i', μA	$+E''_{1/2}$, V	i'', μA	$+E'_{1/2}$, V	i', μA	$+E''_{1/2}$, V	i'', μA
I	H	H	—	—	—	1,55	10,2	—	—	1,53	0,35
			$5 \cdot 10^{-4}$	—	—	1,58	10,2	—	—	1,55	0,25
			$1 \cdot 10^{-3}$	—	—	1,60	10,5	—	—	1,58	0,25
II	NH_2	H	—	0,58	10,2	0,94	11,6	0,56	0,04	0,95	0,15
			$5 \cdot 10^{-4}$	—	—	0,90	18,2	—	—	0,93	0,9
III	H	NH_2	—	0,82	10,7	1,17	12,0	0,80	0,06	1,15	0,4
			$5 \cdot 10^{-4}$	—	—	1,11	19,1	—	—	1,11	0,55
IV	NH_2	NH_2	—	0,42	7,7	0,84	8,2	0,42	0,06	0,86	0,13
			$1{,}25 \cdot 10^{-4}$	0,44	5,0	0,84	9,6	0,43	0,03	0,85	0,25
			$2{,}5 \cdot 10^{-4}$	0,48	2,0	0,84	11,0	0,47	0,02	0,86	0,5
			$5 \cdot 10^{-4}$	—	—	0,84	17,4	—	—	0,84	1,0
			$5 \cdot 10^{-3}$	—	—	0,82	17,5	—	—	0,80	2,1

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*In the presence of perchloric acid.

shifted beyond the limits of discharge of DMF. The addition of acid to a solution of aminobenzimidazole IV leads to a gradual decrease and eventually to the total disappearance (when $c_{HClO_4} = 5 \cdot 10^{-4}$ M) of the first wave; the current of the second wave increases to a value corresponding to the transfer of two electrons, and protonation of the imidazole ring evidently does not occur over the range of selected perchloric acid concentrations. It should be noted that in the case of all of the amino derivatives an increase in the acidity of the medium does not give rise to a considerable change in the potentials of the second waves, since they correspond essentially to oxidation of the cation radicals in neutral solution, the electronic structure of which is similar to the electronic structure of the protonated forms of the molecules. At the acid concentration corresponding to the complete disappearance of the first wave on the disk, a considerable increase in the current of the second wave is observed on the ring; in all likelihood this is associated with the reduction of the hydrogen ions [14] formed as a result of deprotonation of the protonated form of the cation radical.

Thus the results make it possible to conclude that the amino group in amino derivatives of 2-phenylbenzimidazole undergoes oxidation in neutral DMF, whereas the imidazole ring is the reaction center in acidic media.

EXPERIMENTAL

Pure-grade DMF was purified by the method in [15] immediately prior to recording of the voltamperograms. The inert electrolyte was a 0.1 N solution of tetra-n-butylammonium perchlorate. The 2-phenylbenzimidazoles* were crystallized twice from ethanol. The concentration of the compounds was $5 \cdot 10^{-4}$ M. The rotating platinum disk electrode with a ring was constructed as in [16] and had the following characteristics: $r_1 = 1.00$ mm, $r_2 = 1.10$ mm, and $r_3 = 1.13$ mm, and n = 2800 rpm. The efficiency coefficient (N_{eff}) calculated from the results of oxidation of N,N-tetramethyl-p-phenylenediamine in DMF was 0.14. The interior of the electrode was coated with chemically pure fused paraffin for reliable insulation of the disk and ring and to eliminate admission of the electrolyte under the influence of the capillary effect. The electrode was washed successively with a chromic acid mixture, water, aqua regia, water, and chemically pure acetone and air dried immediately prior to recording of the voltamperograms in order to obtain reproducible results on the disk and ring. The reproducibility was ±15 mV. The voltamperograms on the disk were recorded by means of a three-electrode scheme with a P-5848 potentiostat. A modernized LP-7 polarograph with a symmetrical input was used to record the voltamperograms on the ring. A constant

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ring potential for each compound corresponded to the foot of the first oxidation wave on the disk. A saturated calomel electrode served as the comparison electrode. The number of electrons was calculated by comparison with the one-electron wave of N,N-tetramethyl-p-phenylenediamine.

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HETERYLIMIDAZOLES.

VI.* 2-(N,N'-DIMETHYLBENZIMIDAZOLON-5-YL)-4,5-DIARYLIMIDAZOLES

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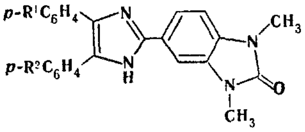
Condensation of 5-formyl-N,N'-dimethylbenzimidazolone with aromatic α-diketones gave 2-(N,N'-dimethylbenzimidazolon-5-yl)-4,5-diarylimidazoles, which are easily oxidized in alkaline media to imidazolyl free radicals. Some of the investigated heterylimidazoles also form radicals when chloroform solutions of them are irradiated. It is shown that the synthesized compounds are inhibitors of the thermal oxidative destruction of polyethylene oxide.

We have previously [1] investigated 4(5)-(N,N'-dimethylbenzimidazolon-5-yl)-2,5(4)-diarylimidazoles. The present paper is devoted to the synthesis and study of the properties of 2-DMBI-4,5-diarylimidazoles (I-XII).†



I-XII

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*See [1] for communication V.

†The abbreviation "DMBI" stands for N,N'-dimethylbenzimidazolon-5-yl.

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