POLAROGRAPHIC STUDY OF HALOGEN AND MERCURY SUBSTITUTED 1,3-OXAZOLES

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A study is made of the polarographic behavior of some halogen and mercury derivatives of phenyloxazoles. By considering the mechanism of electroreduction, it is ascertained, that, the first polarographic wave corresponds to reduction of the halogen or mercury-containing substituent, and the second to reduction of the heterocyclic ring. By analysis of polarographic data it is shown that the electron density sequence for carbon atoms in the oxazole ring is C-2 < C-5 < C-4.

Study of electrophilic substitution reactions showed [1–3] that the electron density in the oxazole ring, which under certain conditions exists as the oxazolium cation, lies in the order C-5 > C-4 > C-2. However these results did not enable conclusions to be drawn regarding relative distribution of electron density in the nonionized heterocyclic ring. Polarographic investigation of the appropriate series of substituted oxazoles gives definite information regarding the nonionized form.

It was previously shown [4, 5] that oxazole derivatives with aryl substituents at positions 2 and 4, or 2 and 5, are respectively reduced at the mercury dropping electrode at group C=N and C=C, giving 4-electron waves, or at groups C=N, C=C, and C—O, giving 6-electron waves. Furthermore the oxazole derivatives show hydrogen catalytic waves.

The present paper sets out the results of an investigation of the polarographic behavior of 1, 3-oxazole derivatives, having in addition to phenyl substituents in the oxazole ring, substituents at the 2, 4, 2, 5, and 4, 5 positions, which are either halogens or contain mercury. For comparison, a study is made of 4, 5-diphenyl-, 2-(4-bromophenyl)-5-phenyl- and 2-bromomethyl-5-phenyl-1,3-oxazoles, hitherto not investigated polarographically.

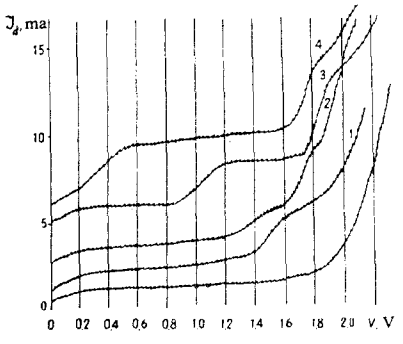


Fig. 1. Polarographic waves of some 1, 3-oxazole halogen derivatives (compounds numbered as in table); 1) XVII, C = 0.38 mM/l, E_a = −0.33 V; 2) XI, C = 0.26 mM/l, E_a = −0.33 V; 3) V, C = 0.30 mM/l, E_a = = −0.31 V; 4) VI, C = 0.28 mM/l, E_a = = −0.34 V.

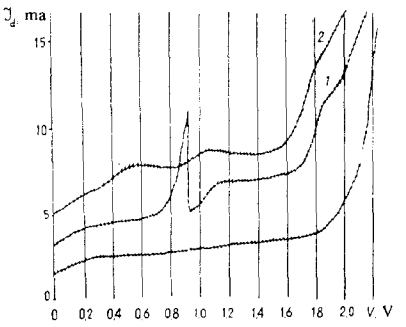
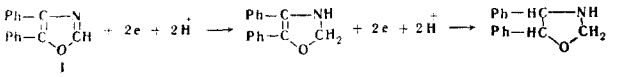
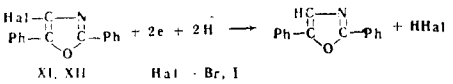


Fig. 2. Polarographic waves of some oxazoles having mercury-containing substituents (compounds numbered as in table); 1) VII, C = 0.48 M/l; E_a = −0.30 V, 2) XIII, C = 0.98 M/l, E_a = = −0.27 V.

The table and Figs. 1 and 2 give the results obtained. The table shows that phenyl substituted oxazoles (I, IV, IX) are reduced by diverse mechanisms at the mercury electrode. Polarographic reduction of IV, IX, XV has already been considered [4, 5]. For I we found only one 4-electron wave, belonging to reduction of the C=N and C=C bonds of the oxazole ring. Like IV, and unlike IX, there is, as follows from the values of n (see table) no scission of the C—O bond in I:



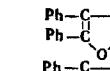
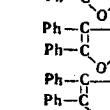
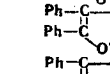
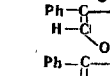
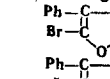
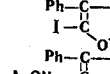
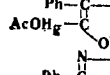
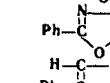
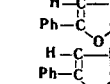
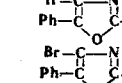
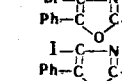
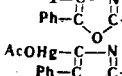
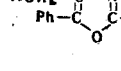
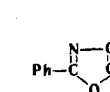
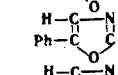
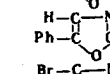
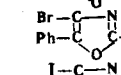
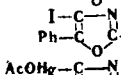
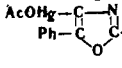
All the oxazole halogen derivatives give two polarographic waves (Fig. 1). The first of these, at a potential of −0.6 to 1.8 volts, is absent for the corresponding oxazole derivatives not containing halogen. The half-wave potential for this wave changes on changing the halogen, moving to positive values on passing from bromine to iodine. Obviously, in the molecules of the oxazole halogen derivatives reduction of the C—Hal bond is characterized by the first wave, this bond, as in other organic compounds [6] being reduced by a 2-electron mechanism, e.g.:



XI, XII Hal – Br, I

From the table it follows that the facility of reduction of the C—Hal bond in oxazoles rises in the order Hal—C-4 < Hal—C-5 < Hal—C-2, showing that the carbon atoms are unequal. Here the clearest difference is found between the C-4 position, on the one hand, and the positions C-5 and C-2 on the other, which

Polarographic Characteristics of 1, 3-Oxazole Derivatives

Compound number	Compound*	$E_{1/2}$, V (relative to the normal calomel electrode		$K_d = \frac{I_d}{Cm^{2/3}\tau^{1/6}}$		$n = \frac{K_d}{607 \cdot D^{1/2}}$ **	
I		—	−2.23	—	5.6	—	3.8 (4)
II		−0.62	−2.26	2.5	4.5	2.0 (2)	3.5 (4)
III		−1.02	−2.27	2.2	4.8	2.1 (2)	4.0 (4)
IV		—	−2.16	—	6.2	—	4.2 (4)
V		−1.31	−2.13	3.5	6.9	2.2 (2)	4.8 (4)
VI		−0.67	−2.08	3.4	5.7	2.4 (2)	4.1 (4)
VII		−1.21	−2.09	2.2	4.9	1.8 (2)	4.0 (4)
VIII		−1.23	−1.93	4.7	9.5	4.2 (4)	8.4 (8)
IX		—	−2.07	—	8.0	—	5.5 (6)
X		−1.75	−2.00	3.6	8.5	2.6 (2)	6.3 (6)
XI		−1.69	−2.03	3.0	6.8	2.1 (2)	4.7 (4)
XII		−1.02	−1.92	3.4	5.8	2.4 (2)	4.2 (4)
XIII		−0.67 −1.21	−1.91	0.7 0.7	7.0	0.6 (1) 0.6 (1)	5.8 (6)
XIV		−1.80	−2.00	4.4	14.5	3.9 (4)	12.8 (12)
XV		unreduced					
XVI		−0.57	—	2.6	—	1.8 (2)	—
XVII		−1.83	—	3.3	—	2.3 (2)	—
XVIII		−1.14	—	3.6	—	2.6 (2)	—
XIX		−0.40 −0.77	(ill-defined wave) −1.90	1.1	4.7	0.9 (1)	3.9 (4)

*Ac = CH_3—CO; Ph = phenyl group.

**Rounded off values of n are given in parentheses.

are very alike with respect to polarographic properties. Replacement of a phenyl group at C-2 by methyl, makes reduction of C-4 halogen even more difficult, as would be expected from its positive inductive effect. Hence, the most electrophilic center in the oxazole ring is C-2, and the order of increasing electron density of the oxazole ring carbon atoms is C-2 < C-5 < C-4. At the same time, the oxazole ring carbon atoms' reactivities change to another sequence, for electrophilic, subsitution reactions, viz. C-2 < C-4 < C-5, obviously due to the formation under those conditions of an oxazole cation with the corresponding heterocyclic ring electron distribution.

Considering the effect of the oxazole ring as a substituent on the half-wave potential of C—Br in phenyl or alkyl, it can be seen that in oxazole **X**, where the bromine atom is in the phenyl group, or in **XVI**, where the bromine atom is linked to an alkyl group, the half-wave potentials corresponding to reduction of the C—Br bond are considerably lower than those of, for example, bromobenzene [7], p-bromodiphenyl [8], or of bromoalkylaryls [7] and bromoalkyls [7], but are approximate to the values of the half-wave potentials of alkyl bromides containing powerful electron-accepting groups. Hence, the electronic effect of the oxazole ring as a substituent in a benzene ring or in an alkyl chain is an electron-accepting one.

The second polarographic wave of the halogenoxazoles lies inside the limits of the reduction potentials of unsubstituted phenyloxazoles (−1.9 to −2.2 V) and it is not very sensitive to the nature of the halogen or its position in the oxazole molecule. To all appearances this wave characterizes the reduction of the heterocyclic part. Though formally $E_{1/2}$ for the second waves of all halogen derivatives should coincide with $E_{1/2}$ of the corresponding unsubstituted oxazole, actually, as can be seen from the table, they are rather more positive than $E_{1/2}$ for the unsubstituted oxazole. This is obviously connected with the effect of the halogen anions at the double electric layer formed during electrolysis. For all the halogen-substituted oxazoles investigated, independent of the positions of the substituents in the heterocyclic ring with respect to one another, the wave proves to be a 4-electron one, but it is absent for **XVI**, **XVII**, and **XVIII**, as the corresponding unsubstituted oxazole **XV** itself behaves as a polarographically inactive compound.

Oxazole derivatives with mercury acetate substituents in the heterocyclic ring are reduced at a mercury dropping electrode to give one 2-electron, or two 1-electron waves, in addition to waves characterizing reduction of the heterocyclic ring. By analogy with reduction of other organomercruy compounds [9, 10], these waves can be ascribed to reduction of the mercury-containing substituent according to the equation

$$CH_3COOHg-R+e+H^+ \rightarrow R-Hg+CH_3COOH$$
$$R-Hg+H^++e \rightarrow RH+Hg,$$ where R = diphenyloxazolyl.

Two-electron waves arising when oxazolylmercury derivatives III, VII and VIII are reduced are distorted by polarographic maxima, and addition of gelatin to the solution under investigation leaves these maxima practically unenlarged (Fig. 2, curve 1).

Still another 4-or 6-electron wave is observed with oxazolyomercury compounds, in the region of potentials of reduction of unsubstituted phenyloxazoles, and in all probability this is characteristic of reduction of the oxazole part.

The polarographic behavior of dioxazolylmercury compounds VIII and XIV is characterized by two complex waves, one of which, a 4-electron one at lower potentials, obviously belongs to the reduction of the mercury substituent, while the second, an 8- (VII) or 12-electron one (XIV), corresponds to the reduction of two oxazolyl rings.

EXPERIMENTAL

All the compounds here investigated were synthesized and purified as described in [1, 2]. The polarographic measurements were made with a LP-55A polarograph and a sensitive mirror galvanometer, $\sim 1.5 \cdot 10^{-9}$ a/mm. The capillary used had the following properties: m = 1.96 mg/sec, τ = 3.8 sec (without applied potentials). The base electrolyte was 0.02 N Et_4NI in 92% MeOH. Standard solutions of the compounds studied were prepared in a 30% benzene−70% MeOH mixture, concentration $\sim 10^{-2}$ mole/l. An electrolyzer with an internal anode, whose potential was checked against a saturated calomel electrode was employed.

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