A POLAROGRAPHIC STUDY OF DIHYDRONAPHTHOXAZOLES

V. D. Bezuglyi, N. P. Shimanskaya, and I. F. Mikhailova

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 1, pp. 26–29, 1968

UDC 543.253:547.659.621'787

The polarographic behavior of four dihydronaphthoxazoles that have not been studied previously has been investigated. It has been shown that the dihydronaphthoxazoles are reduced at higher positive potenials than the corresponding diaryloxazoles because of the increase in conjugation of the substituent in position 5 with the oxazole nucleus. The mechanism of the reduction of dihydronaphthoxazoles is similar to that of the reduction of diaryloxazoles.

Dihydronaphthoxazoles are analogs of diaryloxazoles, the polarographic behavior of which we have studied previously [1]. An investigations of the polarographic characteristics of the dihydroöxazoles was of definite interest for the further elucidation of the influence of structure on the reduction of heterocyclic compounds.

The polarographic behavior of compounds in which a nitrogen-containing heterocyclic nucleus is condensed with an aromatic nucleus has been discussed repeatedly. As examples we may mention quinoline [2], acridine [3], and papaverine [4]. In all the cases mentioned, it was shown that the heterocyclic nucleus of the molecule undergoes reduction first.

The polarographic behavior of dihydronaphthoxazoles has not been studied previously but it was to be assumed that the electroreduction of this series of compounds would take place at the oxazole nucleus first, i.e., the dihydrooxazoles would behave similarly to the diaryloxazoles at a dropping mercury electrode.

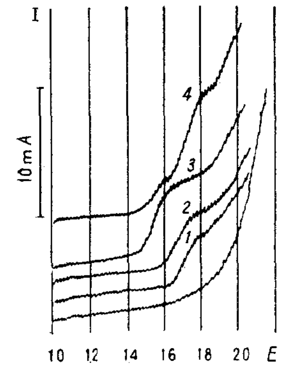


Fig. 1. Polarographic waves of dihydronaphthoxazoles on a background of 0.02 N $N(C_2H_5)_4I$ in 92% methanol: 1) 2-(4-methoxyphenyl)-3', 4'-dihydronaphth-1', 2': 5, 4-oxazole, c = 0.34 mM/l, $E_a = -0.32$ V; 2) 2-phenyl-3', 4'-dihydronaphth-1', 2': 5, 4-oxazole, c = 0.27 mM/l, $E_a = -0.32$ V; 3) 2-(4-biphenylyl)-3', 4'-dihydronaphth-1', 2': 5, 4-oxazone, c = 0.63 mM/l, $E_a = -0.33$ V; 4) 2-phenyl-3', 4'-dihydronaphth-1', 2': 4, 5-oxazole, c = 0.63 mM/l, $E_a = -0.33$ V.

We studied the polarographic behavior of the isomeric 2-phenyl-3', 4'-dihydronaphth-1', 2': 4, 5- and 2-phenyl-3', 4'-dihydronaphth-1', 2':5, 4-oxazoles and some of their derivatives. The polarographic characteristics of the compounds that we studied are given in the table. For comparison, the same table gives the characteristics of some diaryloxazoles studied previously [1].

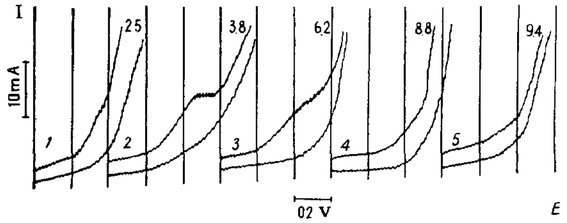


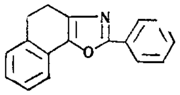
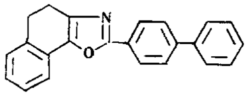
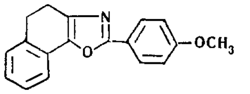
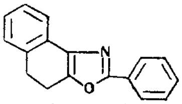
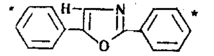
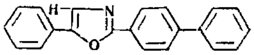
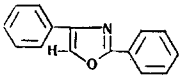
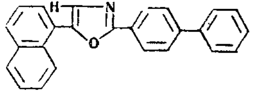
Fig. 2. Polarographic waves of 2-(4-biphenylyl)-3', 4'-dihydronaphth-1', 2':5, 4 oxazole on a background of buffer solutions: 1—$E_{init} = -1.0$ V; 2—$E_{init} = -1.2$ V; 3—$E_{init} = 1.4$ V; 4—$E_{init} = -1.6$ V; 5—$E_{init} = -1.8$ V.

A comparison of the number of electrons consumed in the reduction of the molecules of the substances shows that the dihydronaphthoxazoles are reduced by the same mechanism as the diaryloxazoles [5]. In the majority of cases the $-C{=}N-$, $-C{=}C-$, and $-C-O-$ bonds of the heterocycle are reduced, forming one six-electron wave (Fig. 1). Only in the case of 2-phenyl-3', 4'-dihydronaphth-1', 2':4, 5-oxazole (IV, see table), is the wave split. The first two-electron wave apparently corresponds to the reduction of the $-C{=}N-$ bond, and the second four-electron wave to the simultaneous reduction of the $-C{=}C-$ and $-C-O-$ groups.

The fact that the $-C{=}N-$ bond of the heterocycle is reduced first is shown by the dependence of $E_{1/2}$ on the pH of the medium. A study of the polarographic reduction of compound II on a background of Izmailov-Pivneva buffer solutions [6] has shown that although the waves are poorly expressed (Fig. 2), a shift in the half-wave potential in the positive direction on passing to stronger acid solutions can be observed. For example, at pH 6.2 $E_{1/2} = -1.7$ V and at pH 3.8 $E_{1/2} = -1.6$ V.

A comparison of the ultraviolet absorption spectra [7] of the 2-substituted 3', 4'-dihydronaphth-1', 2':-5, 4-oxazoles and the spectra of the corresponding 2-substituted 5-phenyloxazoles has shown that the introduction of the $-CH_2-CH_2-$ grouping connecting the 5-phenyl and the oxazole rings leads to some bathochromic shift of the long-wave absorption bands

Half-Wave Potentials, Diffusion Current Constants, and Number of Electrons Consumed in the Reduction of the Dihydronaphthoxazoles

Compound	Formula	$E_{1/2}$, V	K_d, mA/mm	n (from the Ilkovič equation)
I		−1.97	9.2	6.1 (6)
II		−1.87	7.5	5.7 (6)
III		−2.03	9.3	6.5 (6)
IV		−1.88; −2.04	3.3; 6.2	2.3 (2); 4.5 (4)
V		−2.07	8.0	5.5 (6)
VI		−1.92	7.8	5.7 (6)
VII		−2.16	6.2	4.2 (2)
VIII		−1.91	7.7	5.8 (6)

---

*For the diaryloxoazoles, only $E_{1/2}$ for the diffusion waves is given.

(20–30 nm) which apparently reflects an increase in the conjugation between the benzene and oxazole nuclei as a result of a decrease in the angle between the planes of these nuclei.

We have shown that in the case of the diaryloxazoles the replacement of a substituent in position 5 has practically no influence on the half-wave potential, as can be seen, for example, from a comparison of compounds VI and VIII. This indicates the weak conjugation of the substituent in position 5 with the oxazole ring. A comparison of compound 1, the molecule of which has the oxazole and pyridine rings connected through a $-CH_2-CH_2-$bridge, with 2,5-diphenyloxazole (V) shows that the half-wave potential of I is more positive than that of compound V. A similar picture is observed in a comparison of compounds II and VI. This shows the improvement of conjugation in the molecules of the dihydronaphthoxazoles as compared with the diaryloxazoles. A particularly pronounced shift of the half-wave potential in the positive direction is found in a comparison of 2-phenyl-3,4-dihydronaphth-1',2':4,5-oxazole (IV) and 2,4-diphenyloxazole (VII), $\Delta E_{1/2}$ in this case being 0.28 V. In compound IV, the $-CH_2-CH_2-$group can be regarded as a substituent in position 5 of the oxazole nucleus. It was stated previously that a substituent in position 5 of the diaryloxazoles has very little effect on the reduction of the $-C{=}N-$ grouping, and therefore the induction effect of the $-CH_2-CH_2-$ group has practically no influence on the half-wave potential of 2-phenyl-3',4'-dihydronaphth-1',2':4,5-oxazole, and the latter has the most positive reduction potential of the series of dihydronaphthoxazoles studied.

Substituents in position 2 of the oxazole nucleus have a substantial effect on the half-wave potential of the dihydronaphthoxazoles, as is the case with the diaryloxazoles [1]. For example, the replacement of a phenyl radical by a biphenylyl radical (compounds I and II) leads to a shift of $E_{1/2}$ in the positive direction by 0.10 V. However, if we compare the half-wave potentials of V and VI it can be seen that in the case of the diaryloxazoles $\Delta E_{1/2}$ is 0.15 V. Thus, the sensitivity of the reaction center to the action of substituents is lower in the case of the strongly conjugated system of the dihydronaphthoxazoles than in the case of the diaryloxazoles.

This phenomenon can apparently be explained by the so-called "dispersion of the conjugation effect" which is the name which V. I. Izmail'skii gives to the decrease in the polarization effect, the mutual influences, and the electronic shifts as a result of ring formation, branching, or the overlapping of systems of conjugation [8].

A methyl group introduced into the para position of the phenyl radical interferes with reduction, shifting $E_{1/2}$ by 0.06 V as compared with the unsubstituted 2-phenyldihydronaphthoxazole.

Thus, on the basis of polarographic and spectroscopic studies of the dihydronaphthoxazoles it has been established that conjugation in the molecules of the latter is greater than in the corresponding diaryloxazoles. This is shown by the positive shift of the half-wave potentials and the bathochromic displacement of the long-wave absorption bands [7].

EXPERIMENTAL

The polarographic measurements were carried out on a LP-55A polarograph with a sensitivity of the mirror galvanometer of $\sim 1.5 \cdot 10^{-9}$ A/mm. The capillary used has the following characteristics: m = 1.96 mg/sec, τ = 3.8 sec (without an applied voltage). The background used was a 0.02 N solution of $N(C_2H_5)_4I$ in 92% methanol. The measurements were carried out in an electrolyzer with an internal anode, the potential of which was determined with respect to a saturated calomel electrode. All the substances studied were synthesized and purified as described by Izmail'skii [7].

REFERENCES

1. V. D. Bezuglyi and N. P. Shimanskaya, ZhOKh, 31, 3160, 1961.
2. I. Pech, Coll., 6, 121, 1934.
3. R. C. Kaye and H. I. Stonehill, J. Chem. Soc., 27, 1951.
4. V. D. Bezuglyi, ZhOKh, 24, 2190, 1954.
5. V. D. Bezuglyi, N. P. Shimanskaya, and E. M. Peresleni, ZhOKh, 34, 3540, 1964.
6. N. A. Izmailov and F. A. Pivneva, Nauchn. zap. Khar'kovsk. inst. sov. torgovli, 1, 41, 121, 1940.
7. N. N. Vorozhtsov, jr. and I. F. Mikhailova, KhGS [Chemistry of Heterocyclic Compounds], 136, 1966.
8. V. I. Izmail'skii, Khim. nauka i prom., 3, 232, 1958.

11 April 1966

All-Union Scientific Research
Institute for Monocrystals, Scintillation Materials, and Particularly Pure Chemical Substances,
Khar'kov