HETERYLIMIDAZOLES

III.* POLAROGRAPHIC OXIDATION OF 2-HETERYL-4,5-DIARYLIMIDAZOLE ANIONS

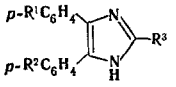
Yu. A. Rozin, V. E. Blokhin, Z. V. Pushkareva, and V. I. Elin

UDC 543.253:547.785.1

The anions of 2-quinolinyl- and 2-(9-acridinyl)-4,5-diarylimidazoles were subjected to polarographic oxidation. The linear relationship between the half-wave potentials and the σ substituent constants was investigated.

Information regarding the effect of nitrogen-containing heterocycle residues on polarographic oxidation is absent in the data on the polarographic oxidation of triarylimidazoles [2], their anions [3, 4], and heteroanalogs of triarylimidazoles containing furan and thiophene residues [5].

We have previously synthesized a number of heteroanalogs of triarylimidazoles (Ic-VIIIa-d, Table 1) containing isomeric quinolinyl and 9-acridinyl groups as substituent R^3 [1, 6]. Oxidation of their anions with potassium ferricyanide gives the corresponding radicals, which recombine in the dark at room temperature to diimidazolyls, which display photochromism and thermochromism owing to reversible dissociation into radicals [1].



Ic-VIIIa-d

Inasmuch as the polarographic oxidation of triarylimidazole anions also gives radicals [3], it was expedient to use this method to establish the quantitative relationship between the chemical structure of imidazole anions Ic-VIIIa-d and their ability to form radicals. The volt-ampere curves of the anions undergoing oxidation have a single wave with a half-wave potential ($E_{1/2}$) ranging from 0.335 to 0.61 V (Table 1). The anions of VIIb-VIId, for which this wave is expressed weakly and lies on the boundary of the background operating characteristics, constitute an exception to this.

As expected, electron-donor substituents facilitate oxidation of the anions, while electron-acceptor substituents hinder oxidation. A linear relationship, which is expressed by the following equations for the series, exists between the oxidation potentials and the overall constants of the para substituents of the phenyl rings in the 4 and 5 positions: III $\Delta E_{1/2} = 0.141\Sigma\sigma$ ($r = 0.945$, $s = 0.003$), V $\Delta E_{1/2} = 0.135\Sigma\sigma$ ($r = 0.991$, $s = 0.008$), VI $\Delta E_{1/2} = 0.122\Sigma\sigma$ ($r = 0.992$, $s = 0.012$), and VIII $\Delta E_{1/2} = 0.105\Sigma\sigma$ ($r = 0.996$, $s = 0.007$).

On examination of the effect of substituents in the 2 position it is apparent that the oxidation potential decreases in the following direction: phenyl > α-naphthyl > β-naphthyl > 9-anthracenyl.

On passing from α- and β-naphthyl- and 9-anthracenyl-substituted anions to their aza analogs (Ic-VIIIc), the oxidation potential increases because of the electron-acceptor effect of the nitrogen atom. It follows from a comparison of the data of series VIII and III that 9-acridinyl is a stronger acceptor than 4-quinolinyl.

*See [1] for communication II.

S. M. Kirov Ural Polytechnic Institute, Sverdlovsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 990-992, July, 1974. Original article submitted July 24, 1973.

TABLE 1. Half-Wave Potentials of the Oxidation ($E_{1/2}$, V) of 2-Heteryl-4,5-diarylimidazole Anions (Ic-VIIIa-d)*

Compound	R³	$R^1=R^2=CH_3O$	$R^1=R^2=CH_3$	$R^1=R^2=H$	$R^1=R^2=Br$	$R^1=H$, $R^2=NO_2$
		a	b	c	d	e
I	2-Quinolinyl	—	—	0,610	—	—
II	3-Quinolinyl	0,340	0,406	0,475	—	—
III	4-Quinolinyl	0,435	0,470	0,490	0,570	0,625
IV	5-Quinolinyl	—	0,413	0,460	—	—
V	6-Quinolinyl	0,335	0,380	0,427	0,470	0,525
VI	7-Quinolinyl	0,350	0,400	0,450	0,490	0,520
VII	8-Quinolinyl	0,600	>0,6	>0,7	>0,7	—
VIII	9-Acridinyl	0,472	0,505	0,540	0,580	—

*For 2,4,5-triphenylimidazole anions (IX), $E_{1/2} = 0.465$ V, while $E = 0.450$ and 0.435 V, respectively, for 2-(α-naphthyl)- and 2-(β-naphthyl)-4,5-diphenylimidazoles (X and XI); $E_{1/2} = 0.430$ V for 2,9-anthracenyldiphenylimidazole (XII).

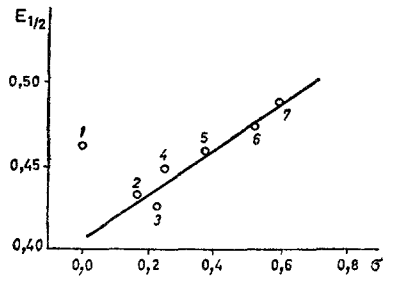


Fig. 1. Correlation between the oxidation potentials of anions IIc-VIc, IX, and XI and the σ-substituent constants: 1) IX; 2) XI; 3) Vc; 4) VIc; 5) IVc; 6) IIc; 7) IIIc.

A linear relationship between $E_{1/2}$ and the σ constants of isomeric quinolinyls, which is expressed by the equation $E_{1/2} = 0.410 + 0.133\sigma$ ($r = 0.951$, $s = 0.007$), except for the point corresponding to anion Ic, is observed in the series of anions of 2-heteryl-4,5-diphenylimidazoles containing isomeric quinolinyl residues (Fig. 1). The increased $E_{1/2}$ value (0.61 V) for anion Ic is probably due to the peculiar ortho effect of the nitrogen atom of 2-quinolinyl. 8-Quinolinyl-substituted imidazoles have unexpectedly high oxidation potentials, if one proceeds from the value of the σ constant [7] of this substituent (−0.06). The high oxidation potential here apparently is determined in many respects by the effect of the field of the nitrogen atom of the quinolinyl substituent. The high negative potentials are apparently the reason that prevents the preparative oxidation of anions Ic and VIIa-d by the action of potassium ferricyanide [6].

It should be noted that the point of IX corresponding to the triphenylimidazole anion also lies above the correlation line. This is probably due to the increased stabilization of the resulting radicals, which contain a two-ring substituent; this is not taken into account by the available σ-substituent constants [7].

EXPERIMENTAL

The polarographic oxidation was carried out with a rotating carbon electrode relative to a saturated calomel half-cell in a thermostated (25 ± 0.2°) cell in dioxane solution containing a borate buffer (pH 9.18). The dioxane–buffer volume ratio was 3:2, and the depolarizer concentration was 10^{-3} M. The rate of rotation of the electrode was 632 rpm, and the area of the carbon electrode was 3.4 mm². The polarograms were recorded by means of a 1P-60 polarograph. The half-wave potentials were found graphically by semilogarithmic treatment of the normalized polarographic curve. The accuracy in the determinations was ± 0.005 V.

The σ constants of isomeric quinolinyls were taken from [7], while those for the remaining compounds were the Jaffe values [8].

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