POLAROGRAPHIC OXIDATION OF TRIARYLIMIDAZOLES

V. N. Shishkin, B. S. Tanaseichuk,
L. G. Tikhonova, and A. A. Bardina

UDC 547.785.1 : 543.253

Ten series of triarylimidazoles were subjected to polarographic oxidation. It was found that electron-donor substituents facilitate polarographic oxidation, while electron-acceptor substituents hinder it. Correlation equations in coordinates of $E_{1/2}$ and σ^+ were found for all of the investigated series.

Despite the numerous investigations of the chemistry of substituted imidazoles, the amount of study devoted to the capacity of these compounds for oxidation has clearly been inadequate [1, 2]. Since triarylimidazoles can form free radicals on oxidation, finding the dependence between the structure and ease of oxidation of triarylimidazoles would make it possible to some degree to predict the character of the effect of substituents on the ease of formation of free radicals of this class. The aim of the present research was an investigation of the effect of substituents on the magnitude of the half-wave potentials for the oxidation of a number of triarylimidazoles. Ten series of substituted triarylimidazoles, which differ with respect to the character, position, and number of substituents in the molecule, were subjected to polarographic oxidation (see Table 1).

It is seen from the data presented in Table 1 that the introduction of electron-donor substituents facilitates polarographic oxidation, while the introduction of electron-acceptor substituents hinders it. The oxidation half-wave potentials range from 0.54 to 1.40 V.

The difference in the oxidation potentials of imidazoles that have identical substituents in the phenyl rings of the 2 and 4 positions is usually insignificant, but it is manifested quite distinctly when substituents with a strong electron-donor effect are present. Thus the introduction of a methoxy group into the phenyl ring of the 2 position of the imidazole ring (VIII) lowers the oxidation half-wave potential more significantly [as compared with triphenylimidazole (I)] than the introduction of a methoxy group into the phenyl ring of the 4 position (XXIV).

Replacement of a phenyl ring by a two-ring hydrocarbon residue (diphenylyl and naphthyl) in the triphenylimidazole molecule hinders the determination of the limiting current. In this connection, the oxidation of diphenylyl- and naphthyldiarylimidazoles was carried out in anhydrous dimethylformamide (DMF), which lowers the oxidation potential by 0.10-0.15 V as compared with 99% aqueous DMF ($E_{1/2}$ of triphenylimidazole is 0.98 V in anhydrous DMF and 1.12 V in 99% aqueous DMF).

To study the effect of substituents on the ease of polarographic oxidation of triarylimidazoles, one can use correlation equations of the Hammett type, which have also found application in polarography [3, 4]. In the general case, the change in the half-wave potential induced by the introduction of a substituent into the molecule is described by the equation

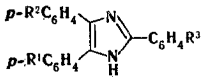
$$E_{1/2}=E^{\circ}_{1/2}+\rho\sigma^{+}.$$

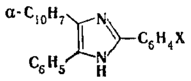
The electrophilic constants of Brown and Okamoto [5] were used to correlate the half-wave potentials of the oxidation of the triarylimidazoles. The results of the correlation are presented in Table 2. It is apparent from a comparison of series 1 and 2 that in the case of triphenylimidazoles, substituents in the phenyl ring of the 2 position have a somewhat greater effect than substituents of the phenyl ring of the 4(5) position. This can be explained if one takes into account the fact that the phenyl rings of the 4 and 5 positions

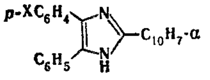
---

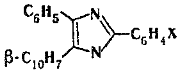
N. P. Ogarev Mordovskii State University, Saransk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 387-390, March, 1973. Original article submitted June 4, 1971.

TABLE 1


Series 1-7


Series 8


Series 9


Series 10

R	Series						
	1	2	3	4	5	6	7
R^1	H	H	CH_3	OCH_3	Br	C_6H_5	H
R^2	H	X	H	H	Br	H	X
R^3	X	H	X	X	X	X	p-C_6H_5

TABLE 2. Characteristics of the Polarographic Oxidation of Triarylimidazoles

Series	Compound	X	$E_{1/2}$*, V	i_d,† μA	b,‡ mV	Correlation parameters
1	2	3	4	5	6	7
1	I	H	1,12	1,73	160	ρ=0,289 r=0,985 s=0,063
	II	p-CH_3	1,11	1,56	162	
	III	m-CH_3	1,14	1,45	174	
	IV	p-Br	1,23	1,71	155	
	V	m-Br	1,27	1,40	220	
	VI	p-NO_2	1,26	1,73	200	
	VII	m-NO_2	1,35	1,51	248	
	VIII	p-OCH_3	0,958	1,15	98	
	IX	p-$N(CH_3)_2$	0,58	1,18	86	
2	X	p-OC_2H_5	0,998	1,20	130	ρ=0,195 r=0,972 s=0,036
	XI	p-NO_2	1,29	1,49	180	
	XII	p-Cl	1,18	1,51	201	
	XIII	p-Br	1,23	1,58	196	
	XIV	p-I	1,19	1,51	180	
	XV	p-CH_3	1,11	1,33	138	
3	XVI	p-CH_3	1,04	1,18	130	ρ=0,265 r=0,985 s=0,056
	XVII	m-CH_3	1,09	1,00	150	
	XVIII	p-Br	1,15	1,24	210	
	XIX	m-Br	1,16	1,07	174	
	XX	p-NO_2	1,22	1,35	188	
	XXI	m-NO_2	1,22	0,84	164	
	XXII	p-OCH_3	0,93	1,42	140	
	XXIII	p-$N(CH_3)_2$	0,54	1,27	107	
4	XXIV	H	1,01	1,25	134	ρ=0,206 r=0,979 s=0,024
	XXV	p-CH_3	0,98	0,98	120	
	XXVI	m-CH_3	0,98	1,02	126	
	XXVII	p-Br	1,01	1,24	126	
	XXVIII	m-Br	1,05	1,31	144	
	XXIX	p-NO_2	1,10	1,18	148	
	XXX	m-NO_2	1,06	1,29	146	
	XXXI	p-OCH_3	0,88	0,87	118	
	XXXII	p-$N(CH_3)_2$	0,54	0,76	90	
5	XXXIII	H	1,18	1,40	128	ρ=0,231 r=0,981 s=0,020
	XXXIV	p-CH_3	1,15	0,90	165	
	XXXV	m-CH_3	1,18	0,88	132	
	XXXVI	p-Br	1,24	1,04	162	
	XXXVII	m-Cl	1,28	1,14	159	
	XXXVIII	p-NO_2	1,40	1,16	162	
6	XXXIX	H	1,12	1,50	150	ρ=0,152 r=0,956 s=0,001
	XL	p-CH_3	1,08	1,32	132	
	XLI	m-CH_3	1,12	1,23	160	
	XLII	p-OCH_3	1,02	0,96	150	
	XLIII	p-NO_2	1,26	1,57	180	
	XLIV	m-NO_2	1,24	1,82	125	
	XLV	p-Br	1,13	1,78	113	
	XLVI	m-Cl	1,17	2,05	120	
7	XLVII	H	1,11	1,39	150	ρ=0,184 r=0,941 s=0,070
	XLVIII	p-CH_3	1,05	1,27	158	
	XLIX	p-OCH_3	0,98	1,21	159	
	L	p-OC_2H_5	0,99	1,05	160	
	LI	p-Cl	1,16	2,00	135	

TABLE 2 (continued)

1	2	3	4	5	6	7
8	LII	H	1,08	1,89	117	
	LIII	p-CH_3	1,06	1,98	115	
	LIV	m-CH_3	1,08	1,69	100	
	LV	p-OCH_3	1,01	1,41	148	
	LVI	p-Br	1,10	1,86	115	$\rho=0{,}141$
	LVII	m-Cl	1,17	1,77	116	$r=0{,}986$
	LVIII	p-NO_2	1,24	1,89	130	$s=0{,}016$
	LIX	m-NO_2	1,18	1,43	120	
9	LX	H	1,07	1,18	100	
	LXI	p-CH_3	1,04	1,02	130	
	LXII	p-OCH_3	0,96	1,02	98	$\rho=0{,}186$
	LXIII	p-OC_2H_5	0,97	1,02	105	$r=0{,}980$
	LXIV	p-Br	1,10	1,27	110	$s=0{,}039$
	LXV	p-Cl	1,13	1,25	145	
10	LXVI	H	1,09	1,89	125	
	LXVII	p-CH_3	1,08	1,66	122	
	LXVIII	m-CH_3	1,10	1,57	130	$\rho=0{,}155$
	LXIX	p-OCH_3	0,98	1,46	120	$r=0{,}981$
	LXX	p-Br	1,12	2,00	125	$s=0{,}002$
	LXXI	m-Cl	1,18	2,00	125	
	LXXII	p-NO_2	1,22	1,85	128	
	LXXIII	m-NO_2	1,22	2,12	90	

---

* Relative to a saturated calomel electrode.

† Limiting diffusion current.

‡ Slope of the graph of the dependence of log $[(i_d-i)/i]$ on E.

are turned ~ 90° about the $C_{(4)}$—Ar and $C_{(5)}$—Ar bonds, while the phenyl ring in the 2 position is in the same plane with the imidazole ring [6].

The presence and character of the substituents in the phenyl rings of the 4 and 5 positions of the imidazole ring also affect the ρ value, which characterizes the sensitivity of the reaction center to the presence of substituents in the phenyl ring of the 2 position of the imidazole ring — the introduction of a methyl group, bromine, or a methoxy group decreases ρ. Moreover, the most pronounced decrease in ρ is observed when a methoxy group is present (series 4).

When one of the phenyl rings is replaced by a two-ring hydrocarbon residue, the picture changes. In this case, the reaction center is more sensitive to the presence and character of the substituent in the 4(5) position of the imidazole ring (see series 6-7 and 8-9). This sort of difference in the degree of the effect of substituents on introduction of a polycyclic substituent can hardly be explained by specific electrochemical factors, since this peculiarity is not manifested for some one series but is characteristic for all of the investigated series that have a two-ring hydrocarbon residue as a substituent. The more probable explanation here is that based on the difference in the configurations of imidazoles that have two-ring substituents in the 2 and 4(5) positions of the imidazole ring. The introduction of two-ring residues into the 2 position, where they are coplanar with the imidazole ring, promotes the formation of a single electronic system, which is more sensitive to the presence of a substituent than the less developed electronic phenyl—imidazole system, and this also facilitates better manifestation of the effect of substituents in the 4(5) position. However, when the two-ring substituent is in the 5(4) position of the imidazole ring, where it is deflected from the plane of conjugation with imidazole, the effect of a substituent in the 2 position of the imidazole ring on the change in the half-wave potential is manifested to a lesser extent in connection with the less developed system of conjugation; this also leads to larger ρ values in series 7 and 9 than in series 6, 8, and 10.

EXPERIMENTAL

The polarographic oxidation of the triarylimidazoles was carried out with a rotating platinum electrode in a thermostatted cell at 25 ± 0.2°. The rate of rotation of the electrode was 600 rpm, and the electrode area was 0.785 mm². The polarograms were recorded with an LP-60 electronic polarograph. The comparison electrode was a saturated calomel electrode. The electrode potential was monitored with a PPTV-1 potentiometer. The measurements were made in 99% aqueous DMF (series 1-5) and anhydrous DMF (series 6-10) in the presence of 0.1 M $LiClO_4$. The depolarizer concentration was $1 \cdot 10^{-3}$ M. A linear dependence of the diffusion current on the depolarizer concentration was observed for all of the triarylimidazoles.

The volt-ampere curves of the triarylimidazoles have the shape of a well-expressed wave. The volt-ampere curves of the nitro- and bromo-substituted imidazoles display weakly expressed waves with difficult-to-determine limiting currents (i_d). The half-wave potentials for the oxidation of the triarylimidazoles were determined from the dependence of log $[(i_d-i)/i]$ on E; they were reproduced with an accuracy of ± 5 mV. The results of the polarographic oxidation of the triarylimidazoles are presented in Table 1.

The dimethylformamide used as the solvent in this study was purified by shaking with calcined potassium carbonate for 72 h and subsequent vacuum distillation at 38-40° (10 mm). The purity of the DMF was monitored by polarography; a solution of lithium perchlorate in the pure solvent gave a normal charge curve.

The synthesis and characteristics of the investigated imidazoles were described in [7-10].

LITERATURE CITED

1. W. Sümmermann and H. Baumgärtel, Ber. Bunsenges. Phys. Chem., 74, 19 (1970).
2. W. Sümmermann and H. Baumgärtel, Coll. Czech. Chem. Commun., 36, 575 (1971).
3. P. Zuman, Advances in Polarography, Beng. Press (1960), p. 812.
4. V. D. Bezuglyi, V. F. Lavrushin, and G. G. Belous, Zh. Obshch. Khim., 35, 606 (1935).
5. Yu. A. Zhdanov and V. I. Minkin, Correlation Analysis in Organic Chemistry [in Russian], Izd. Rostovsk. Univ. (1966).
6. Yu. A. Kolodyazhnyi, A. D. Garnovskii, S. V. Serbina, O. A. Osipov, B. S. Tanaseichuk, L. G. Rezepova, and S. V. Yartseva, Khim. Geterotsikl. Soedin., 819 (1970).
7. B. S. Tanaseichuk, A. A. Bardina, and V. A. Maksakov, Zh. Organ. Khim., 7, 1508 (1971).
8. A. A. Bardina, B. S. Tanaseichuk, and A. A. Khomenko, Zh. Organ. Khim., 7, 1267 (1971).
9. B. S. Tanaseichuk, A. A. Bardina, and A. A. Khomenko, Khim. Geterotsikl. Soedin., 1255 (1971).
10. B. S. Tanaseichuk, L. G. Rezepova, É. P. Sanaeva, and V. V. Stanovkin, Uch. Zap. Mordovsk. Gos. Univ. im. N. P. Ogareva, Ser. Khim., 81, 79 (1971).