POLAROGRAPHIC OXIDATION OF 2,5-SUBSTITUTED TETRAPHENYLPYRROLES

V. N. Shishkin, S. L. Vlasova,
and B. S. Tanaseichuk

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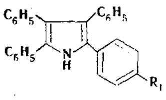
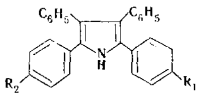
Four series of tetraphenylpyrrole derivatives were subjected to polarographic oxidation. It was found that electron-donor substituents in the p position of the phenyl ring facilitate polarographic oxidation, while electron-acceptor substituents in the p position hinder it. Correlation equations in coordinates of $E_{1/2}$ and σ^+ were found for all four series, and a correlation between the half-wave potential of polarographic oxidation and the logarithm of the rate constants for decolorization of benzene solutions of the corresponding radicals in air was detected.

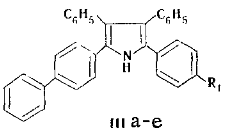
The polarographic oxidation of four series of tetraphenylpyrrole derivatives (I-IV) was investigated to expose the regularities between the chemical structure and properties of compounds of the tetrarylpyrrole series. The results were compared with kinetic data from an investigation of the air stability of benzene solutions of the corresponding radicals. When I-IV are oxidized on a platinum electrode, they give well-expressed one-electron reversible waves. The polarographic characteristics of the oxidation of tetraphenylpyrrole derivatives are presented in Table 1. As seen from Table 1, the introduction of electron-donor substituents facilitates polarographic oxidation of tetraphenylpyrroles I-IV, while electron-acceptor substituents hinder it; this is in agreement with the general regularities in the polarographic oxidation of organic compounds [1]. In series III and IV, the effect of substituents is less appreciable, but the character of their effect is retained.



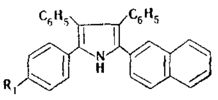
I a-f



II a-g



III a-e



IV a-e

To determine the quantitative principles of the effect of the electronic properties of substituents on the ease of polarographic oxidation, the correlation equations in coordinates of $E_{1/2}$ and σ^+ were found for the investigated compounds (Table 1).

As seen from Fig. 1 and Table 1, there is a satisfactory correlation between the half-wave potentials of polarographic oxidation and the total electrophilic constants (σ^+). The absence of a correlation between $E_{1/2}$ and the Hammett substituent constants is probably explained by the fact that the decisive factor in the polarographic oxidation of tetraphenylpyrrole derivatives is the degree of conjugation of these substituents with the pyrrole ring. This is particularly confirmed by the decrease in the absolute value of the reaction constant (ρ) in the correlation equations when polycyclic hydrocarbon residues are present as substituents (Table 1). A comparison of the results with the kinetic investigations of the destruction of the radicals formed during the oxidation of the corresponding derivatives demonstrates that a lower rate constant for destruction of the radical in benzene solution in air corresponds to the readily oxidized derivatives; this apparently can be explained by the dependence of the oxidation potential of the derivatives on the stability of the radical formed (Table 1 and Fig. 2).

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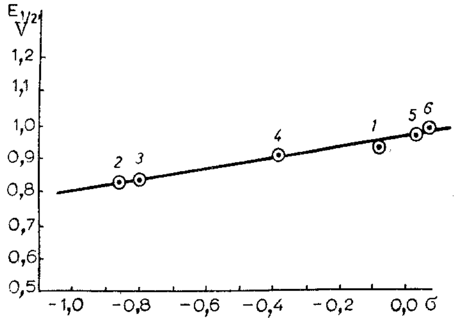

Fig. 1. Half-wave potential of polarographic oxidation of 2-(p-R-phenyl)-3,4,5-triphenylpyrroles (I) as a function of the σ^+ electrophilic substituent constants (ρ = 0.17, r = 0.987, s = 0.04).

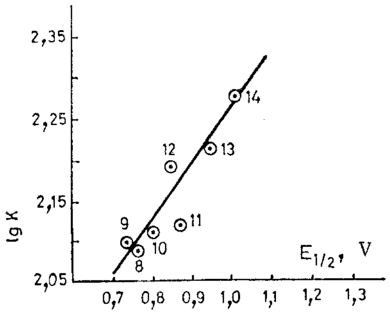

Fig. 2. Logarithm of the rate constants for the decolorization of benzene solutions of 2,5-(p,p'-R_1,R_2-diphenyl)-3,4-diphenylpyrroles (II) as a function of their polarographic oxidation potentials.

TABLE 1. Polarographic Characteristics of the Oxidation of Tetraphenylpyrrole Derivatives in Anhydrous Dimethylformamide

Comp.	R_1	R_2	$E^*_{1/2}$	$i^\dagger_{max}$	b ‡	K^{**}	Parameters of correlation equation
Ia	H	H	0,910	15,36	76	242	ρ=0,17 r=0,987 s=0,04
Ib	OCH_3	H	0,805	19,44	76	161	
Ic	OC_2H_5	H	0,800	19,81	79	192	
Id	CH_3	H	0,877	18,33	75	212	
Ie	Cl	H	0,955	19,81	93	255	
If	Br	H	0,966	14,99	78	273	
IIa	OCH_3	OC_2H_5	0,735	17,96	85	125	ρ=0,15 r=0,989 s=0,05
IIb	OCH_3	OCH_3	0,762	15,92	77	120	
IIc	CH_3	OC_2H_5	0,800	17,40	73	130	
IId	CH_3	CH_3	0,875	19,25	79	133	
IIe	Cl	OCH_3	0,855	17,03	76	154	
IIf	Cl	CH_3	0,950	21,29	82	165	
IIg	Cl	Br	1,008	12,27	68	189	
IIIa	OCH_3	C_6H_5	0,830	17,96	92	163	ρ=0,14 r=0,982 s=0,05
IIIb	OC_2H_5	C_6H_5	0,836	12,03	86	175	
IIIc	H	C_6H_5	0,905	19,44	87	230	
IIId	CH_3	C_6H_5	0,921	14,25	87	185	
IIIe	Cl	C_6H_5	0,962	10,74	100	262	
IVa	OCH_3		0,828	14,81	80	102	ρ=0,13 r=0,980 s=0,05
IVb	OC_2H_5		0,826	12,59	89	110	
IVc	CH_3		0,907	11,11	78	—	
IVd	H		0,922	16,29	78	131	
IVe	Cl		0,943	8,33	84	134	

*Relative to a saturated calomel electrode (in volts).

† The limiting diffusion current in microamperes.

‡ The slope of the polarographic wave in millivolts.

**The rate constants for the destruction of the corresponding radical in benzene in air (in liters per mole per minute).

EXPERIMENTAL

Substituted 2,5-Diaryl-3,4-diphenylpyrroles. These compounds were obtained by Davidson condensation of aryl benzyl ketones and aryl α-hydroxybenzyl ketones with ammonium acetate in glacial acetic acid [2,3]. The polarographic oxidation of the tetraphenylpyrrole was carried out in anhydrous dimethylformamide with a reference electrolyte of 0.1 M lithium perchlorate in a thermostatted cell at 25 ± 0.2°. The indicator electrode was a rotating platinum disc electrode with an area of 0.785 mm^2 and a rate of rotation of about 600 rpm. The polarograms were recorded with an LR-60 electronic recording polarograph. The half-wave potential was determined relative to a saturated calomel electrode and was monitored by means of a PPTV-1 potentiometer. The half-wave potentials were calculated from the graph in coordinates of E and log (i_{max} − i)/i.

Purification of Dimethylformamide. Pure dimethylformamide was shaken with calcined potassium carbonate, filtered, and vacuum distilled to give a product with bp 38-40° (10 mm).

LITERATURE CITED

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2. B. S. Tanaseichuk, S. P. Vlasova, A. N. Sunin, and V. E. Gavrilov, Zh. Organ. Khim., 5, 144 (1969).
3. S. L. Vlasova, B. S. Tanaseichuk, and E. N. Morozov, Zh. Organ. Khim., 7, 1264 (1971).