Synthesis and Polarographic Reduction of 2-Nitro-2′-hydroxyazobenzene Derivatives

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Received August 31, 1970

Accepted for publication February 4, 1971

A number of 4-substituted 2-nitro-2′-hydroxy-5′-methylazobenzenes were prepared by copulation of 4-substituted 2-nitrobenzenediazonium ion with *p*-cresol. The half-wave potentials of the reduction of azo and nitro group were determined over the pH range from 3 to 12. The half-wave potentials extrapolated to pH 0 were correlated with Hammett constants σ_p and σ_m. The dependence of anodic current on pH, depolarizer concentration, commutation frequency, and temperature was established for the commutated polarographic curves. The relationship between drop time and potential throwing light on the course of the adsorption of depolarization product was deduced from measurements.

The derivatives of 2-nitro-2′-hydroxyazobenzene are interesting for two reasons. They may be transformed by reduction into corresponding 2-(2-hydroxyphenyl)benzotriazoles [1—3] which are frequently used as photosensitizers of various materials [4—6]. On the other hand, they contain two functional groups situated in *ortho* position to each other and influenced by the hydroxy group also situated in *ortho* position with respect to azo group which can be easily reduced at the dropping mercury electrode.

Experimental

The substances prepared, their melting points (Kofler), yields, elemental analyses, and R_F values are given in Table 1.

The chromatographic separation of substances was performed on a strewn thin layer of silica gel (40—100 mμ) while absolute chloroform was used for elution.

The polarographic measurements of chromatographically pure substances were made by means of the instrument LP 55 with photographic record, the speed of paper shift 200 mV/min., the abscissas after 100 mV, the height of mercury column 49 cm, the sensitivity 1/100, the temperature 50°C except where otherwise stated. Britton—Robinson buffer solution of 0.04 M concentration in 60% methanol was used as a fundamental electrolyte, the concentration in substances *I*—*IX* was 5×10^{-4} M while the concentration in substance *X* was 1×10^{-4} M. Gelatine was added in the concentration of 2.5×10^{-2} %. The measurements were made in a polarographic vessel with temperature control jacket

Table 1

Substance	X	Formula	M	Calculated/found				Yield [%]	M.p. [°C] (Solvent)	R_F
				% C	% H	% N	% Br			
I	H	$C_{13}H_{11}N_3O_3$	257.25	60.70	4.31	16.33		87	124	0.57
				60.79	4.15	16.11			(ethanol)	
II	CH_3	$C_{14}H_{13}N_3O_3$	271.28	61.98	4.83	15.49		89	144	0.59
				62.20	4.73	15.62			(ethanol)	
III	Br	$C_{13}H_{10}N_3O_3Br$	336.15	46.45	3.00	12.50	23.77	82	163	0.70
				46.60	3.38	12.10	23.74		(ethanol)	
IV	COOH	$C_{14}H_{11}N_3O_5$	301.26	55.81	3.67	13.95		71	260	0.16
				55.80	3.59	13.41			(ethanol)	
V	NH_2	$C_{13}H_{12}N_4O_3$	272.26	57.21	4.44	20.58		88	202	0.53
				56.99	4.27	20.10			(ethanol)	
VI	OCH_3	$C_{14}H_{13}N_3O_4$	291.28	57.72	4.50	14.43		79	152	0.19
				58.10	4.58	14.22			(ethanol)	
VII	CH_3CO	$C_{15}H_{13}N_3O_4$	299.29	59.40	4.32	13.85		84	186	0.26
				59.47	4.27	13.30			(ethanol)	
VIII	CHO	$C_{14}H_{11}N_3O_4$	285.26	58.95	3.89	14.73		71	183	0.29
				58.50	4.05	14.22			(ethanol)	
IX	$COOCH_3$	$C_{15}H_{13}N_3O_5$	319.29	56.42	4.10	13.16		69	246	0.17
				57.20	4.05	12.75			(methanol)	
X	NO_2	$C_{13}H_{10}N_4O_5$	302.25	51.65	3.34	18.54		87	220	0.44
				51.60	3.28	18.16			(acetic acid)	

while fritted glass separated the solution investigated from reference saturated calomel electrode.

The *Kalousek* commutator [7] having the range of 7—40 c s^{-1} was applied to the measurements of anodic current. The concentration in substances *I* and *X* was 1×10^{-4} M and temperature 30°C. The voltage in both producing and recording periods was parallelly raised while $\Delta E = 100$ mV. The pH values were measured with the laboratory compensation pH-meter PHK 1 calibrated by means of standard buffer solutions.

2-Nitro-4-X-2'-hydroxy-5'-methylazobenzene (I—IV, VI—VIII, X)

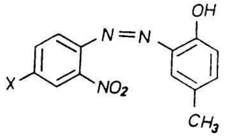
The solution of diazonium salt containing 0.01 mole of corresponding nitroaniline [8] was allowed to drop under intensive stirring into a solution containing 0.01 mole (1.08 g) of *p*-cresol, 1.06 g of sodium hydroxide, and 7.3 g of anhydrous sodium carbonate in 80 ml of water at 10—15°C. The suspension of dye thus formed was allowed to stand for about one hour at room temperature under occasional stirring. The red substance was sucked and washed with water into neutral reaction.

2-Nitro-4-amino-2'-hydroxy-5'-methylazobenzene (V)

The diazotization and copulation were carried out analogously. The azo compound obtained was dissolved in about 100 ml of 10% aqueous solution of sodium hydroxide and heated under reflux for 10—15 minutes. By neutralization the substance *V* was separated. This substance was sucked and washed thoroughly with water.

2-Nitro-4-carbomethoxy-2'-hydroxy-5'-methylazobenzene (IX)

The solution containing 0.01 mole of substance *IV* in 100 ml of absolute methanol was refluxed under constant introduction of gaseous hydrogen chloride for about 45 minutes. On distillating about 50 ml of methanol and cooling, the substance *IX* separated. This substance was sucked and washed with cold methanol.



Results and Discussion

The substances *I*—*X* were reduced at dropping mercury electrode over the pH range from 3 to 12. 2-Hydroxy-5-methylazobenzene, the polarogram of which has a single cathodic wave with half-wave potential $E_{1/2} = +0.061 - 0.064$ pH in the pH range from 3 to 12, was used as a standard substance. It is obvious that the measured cathodic wave corresponds to the reduction of azo group. By introducing a nitro group into the molecule of standard substance (substance *I*) the half-wave potential of azo group reduction shifts to a more positive value $E_{1/2} = +0.171 - 0.059$ pH within the pH range from 3 to 12. Furthermore, in the polarogram of substance *I* a second wave with more negative half-wave potential $E_{1/2} = -0.229 - 0.060$ pH appears at pH values ranging from 3 to 10.

Table 2

Substance	First wave			Second wave			Third wave		
	$E_{1/2}$ pH = 0	$dE_{1/2}/dpH$	pH	$E_{1/2}$ pH = 0	$dE_{1/2}/dpH$	pH	$E_{1/2}$ pH = 0	$dE_{1/2}/dpH$	pH
I	0.171	0.0590	3–12	−0.229	0.0601	3 –10			
II	0.135	0.0579	3–12	−0.210	0.0633	3 –10			
III	0.188	0.0592	3–12	−0.040	0.0719	3 –10	0.083	0.0658	8–10.5
IV	0.233	0.0645	3–12	−0.074 −0.251	0.0798 0.0666	3 – 5.75 6.25–10			
V	0.104	0.0622	3–10	−0.323	0.0624	3 –10			
VI	0.141	0.0556	3–12	−0.111	0.0708	3 –10			
VII	0.233	0.0604	3–12	−0.077	0.0694	3 –10			
VIII	0.279	0.0640	3–12	−0.062	0.0727	3 –10			
IX	0.220	0.0606	3–12	−0.070 −0.238	0.0798 0.0667	3 – 5.75 6.25–10	0.153	0.0710	3– 7
X	0.256	0.0598	3–12	+0.014	0.0646	3 – 9	−0.250	0.0658	3–10

It has been found that the relationship between the diffusion current of the first and second waves and the square root of mercury column height is linear at pH values ranging from 3 to 10 and that the height of the second wave is the double height of the first wave. The second wave, therefore, corresponds to reduction with a twofold number of electrons with respect to the first wave.

It is known that the azo group in *trans* azobenzene is reduced in protolytic solvents in the pH region between 0.6 and 13.75 [9] by two electrons to hydrazobenzene $E_{1/2} = 0.068 - 0.06$ pH and the nitro group in nitrobenzene molecule is reduced in protolytic solvents at pH < 3 by four electrons to phenylhydroxylamine and subsequently by two electrons to aniline. The first four-electron wave has the diffusion character and its half-wave potential is a linear function of pH up to pH 9 [10]

$$E_{1/2} = -0.18 - 0.059\ \mathrm{pH}$$

while the second wave appears only at pH < 5 and has no diffusion character because its height is not a linear function of nitrobenzene concentration. Moreover, its half-wave potential is not a linear function of pH [10]. By comparing the published data with our experimental results on the substance *I* and analogously on the substances *II*—*X* it is possible to attribute the first wave with more positive half-wave potential to the reduction of azo group and the second wave with more negative half-wave potential to the reduction of nitro group in position 2.

The cathodic waves of substance *V* are in the pH region between 3 and 9 partially deformed and indicate splitting to three waves. It may be due to a disproportionation of the hydrazo derivative formed by the reduction in amine and azo compound which may be further reduced [11].

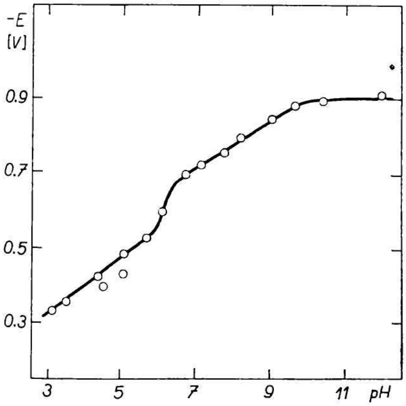


Fig. 1. Dependence of the half-wave potential *E* on pH for the nitro group reduction in substance *IV*, concentration 5×10^{-4} M.

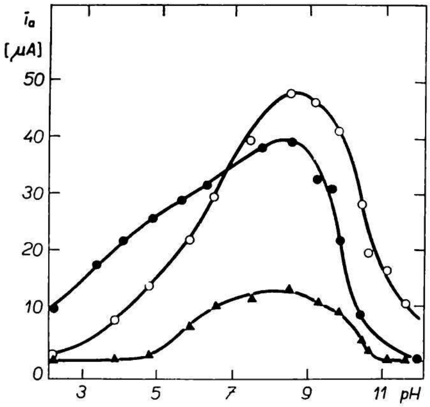


Fig. 2. Dependence of the anodic current i_a of switched curves on pH.
○ substance *X*, oxidation of the depolarization product of azo group; ● substance *I*; ▲ substance *X*, oxidation of the depolarization product of nitro group. Frequency 7 c s^{-1}, $t = 30$°C, concentration of *I* and *X* 1×10^{-4} M, $\Delta E = 100$ mV, gelatine concentration 2.5×10^{-2} %.

The substance *X* is reduced in three waves within the pH range from 3 to 12 (Table 2). Assuming that the reduction of azo group is responsible for the first wave, the subsequent two waves belong to the reduction of two nitro groups. Considering the possibility of the formation of intramolecular hydrogen bond between hydrogen of the hydrazo group and oxygen atom of the nitro group it may be supposed that this association enhances the electrophilic character of nitrogen atom of the nitro group which can thus be reduced at a less negative potential than the nitro group in position 4.

The polarogram of substance *III* shows a very low wave at pH 8—10.5

$$E_{1/2} = 0.083 - 0.065\,\mathrm{pH}$$

similarly to the polarogram of substance *IX* obtained at pH 3—7

$$E_{1/2} = 0.153 - 0.071\,\mathrm{pH}.$$

The origin and character of these waves was not studied. In the case of substances *IV, VII, VIII,* and *IX,* no cathodic wave corresponding to the reduction of $>C=O$ group was recorded under conditions of the measurements.

The dependence of half-wave potential of azo and nitro group reduction on pH was investigated with substances *I*—*X* in the pH range from 3 to 12. By using the method of least squares the equations of straight lines, their slopes and half-wave potentials were computed from the measured values for pH 0 (Table 2). The protonation of the nitro group is preceded by electron reception at pH >10 [10] and for this reason a further increase in pH does not result in any change in half-wave potential.

For substances *IV* and *IX* a rapid increase in the negative value of half-wave potential of the nitro group reduction appears in the pH region between 5.75 and 6.25 (Fig. 1). At about pH 6, the substance *IV* is already fairly ionized what results in a change in electron effect of the substituent — originally COOH group but now COO^- anion. In the case of substance *IX*, the hydrolysis of carbomethoxy group is likely to set in under conditions of the measurements (50°C).

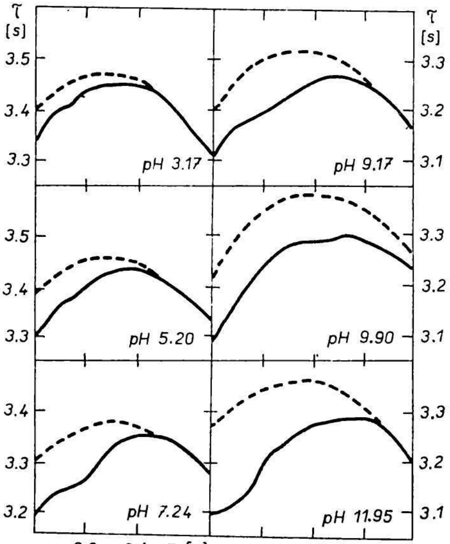


Fig. 3. Dependence of the drop time τ on potential *E* at pH 3—12.
— — — fundamental electrolyte: Britton—Robinson buffer solution 0.04 M; —— substance *I*, concentration 1×10^{-4} M.

It is necessary to state that the slope of cathodic wave of the nitro group reduction decreases for all substances *I*—*X* at pH >10 whereas the wave of the azo group reduction remains unchanged.

The half-wave potentials, extrapolated to pH 0, of the azo and nitro group reduction for substances *I*—*X* are a linear function of the Hammett σ_p and σ_m constants of substituents *X*. By the method of least squares the values of the reaction parameter ϱ were calculated from the slopes of straight lines. It was found that $\varrho = +0.13$ for the azo group reduction and $\varrho = +0.40$ for the nitro group reduction. The nitro group is therefore more affected by electron effect of the substituent *X* than the azo group.

Furthermore, the reversibility of electrode process of the azo and nitro group reduction was investigated for substances *I* and *X* by means of the Kalousek commutator.

The dependence of anodic current i_a of switched curves on pH was measured (Fig. 2). The interesting result following from the values measured shows that the reduction of nitro group in position 2 (substance *X*) is reversible in the pH range between 5 and 11 and that the reversibility of the azo group reduction in substances *I* and *X* is the highest at about pH 8.5—9.5 while *Florence* [12] found that the azo group reduction was the least reversible at about pH 9 in the case of azobenzene and azobenzene-4-sulfonic acid. He explained this fact on the basis of the measured dependence of drop time on potential by assuming adsorption of the reduction product on the dropping mercury electrode.

For substance *I*, the dependence of drop time on potential was measured at pH ranging from 3 to 12 (Fig. 3). It is evident that substance *I* effects the reduction of drop time what is due to the adsorption on mercury drop. The reduction of drop time is not, however, minimum at about pH 9; hence, the adsorption of the depolarization product has no essential effect on the reversibility of electrode reaction in the case of substance *I*.

Moreover, the relationship between the anodic current i_a and the concentration of substance *I* was determined for a few values of pH at the frequency of 7 c s^{-1}. The values obtained suggest that the azo group reduction has the highest degree of reversibility for all concentrations investigated at pH 9, approximately.

The anodic current i_a depending on the switching frequency reaches the highest value at pH 8.2. The dependence of the anodic current i_a on temperature is linear at temperatures ranging from 15 to 50°C. The temperature gradient is -1.63 μA/°C.

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Translated by R. Domanský