

## INFLUENCE OF STRUCTURE OF SOME AZO COMPOUNDS ON THEIR ACID-BASE PROPERTIES AND REDUCTION

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A series of azo compounds were prepared and their acid-base equilibria in aqueous-alcoholic solutions were studied in dependence on the pH. The oxidation-reduction properties of the compounds and of their reduction products were examined polarographically and by preparative electroreduction. The effect of substituents at the azo group on the examined properties of the compounds is discussed.

Papers dealing with the study of azo compounds have been concerned with their use as acid-base, metallochromic indicators or chelating reagents for photometric or extraction-photometric determination of metals<sup>1-4</sup>. Some papers are concerned with spectrophotometric investigation of the acid-base equilibria and examination of the substituent effects on the properties of such reagents<sup>5,6</sup>. Polarographic reduction of azo and heteroazo compounds from the point of view of their reduction mechanism is the subject of the papers<sup>7-9</sup>; they indicate that azo and heteroazo compounds reduce always *via* the corresponding hydrazo compounds, which undergo disproportionation with different rates. The rate of disproportionation of hydrazobenzenes in acidic solutions is so high that the wave height corresponds to four-electron reduction; wave height corresponding to two-electron reduction has been observed only in alkaline solutions, still coulometric measurements point to four-electron reduction in this case too. Florence and coworkers<sup>8</sup>, who have studied the polarographic reduction of pyridyl- and thiazolylazo compounds, found for these substances two-electron waves in acidic solutions and four-electron waves in alkaline solutions.

In the present work, the structure of some azo compounds is related to their acid-base properties based on a comparison of spectrophotometric and electrophoretic measurements.

### EXPERIMENTAL

The compounds I-IV were prepared by diazotization of N,N-diethyl-*p*-phenylenediamine sulphate and successive coupling according to<sup>10-12</sup>, the compound V according to<sup>13</sup>. Diazotization of 2-amino-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole and coupling led to the substances VI (ref.<sup>14</sup>), VII (ref.<sup>15</sup>) and VIII (ref.<sup>16</sup>).

The purity of the substances prepared was tested by melting point measurements, elementary analysis, and paper chromatography<sup>17</sup>. Aminobarbituric acid<sup>18</sup> was prepared by reduction of nitrobarbituric acid, which was synthesized by nitration of barbituric acid<sup>19</sup>. 2-Nitroso-1,3-

-indanedione and 1-phenyl-3-methyl-4-nitrosopyrazolone were prepared by nitrosation<sup>20</sup> of 1,3-indanedione and 1-phenyl-3-methylpyrazolone, respectively. The melting points of the substances prepared agreed well with the published data. The other chemicals used were reagent grade purity. The solutions were prepared from distilled ethanol and redistilled water.

The pH values were measured on a PHM-26 pH-meter (Radiometer, Copenhagen) using a G 202 B glass electrode and a K 401 calomel electrode. The values measured in ethanol-water mixed solutions have not been corrected and the symbol pH has been used for these systems. Spectrophotometric measurements were performed on a Specord UV-VIS recording spectrophotometer (Zeiss, Jena) in aqueous-alcoholic solutions (40% vol. ethanol), ionic strength  $I = 0.1$ , using 1 cm cells. The concentrations were  $4 \cdot 10^{-5} \text{ mol l}^{-1}$  for the compounds *I-IV* and  $2 \cdot 10^{-5} \text{ mol l}^{-1}$  for the compounds *V-VIII*.

Polarographic measurements were performed in a Kalousek's vessel with separate S.C.E. using an OH-102 polarograph (Radelkis, Budapest). The preparative electroreduction was carried out as described in the paper<sup>21</sup>. Electrophoretic measurements were performed in an apparatus after Jokl<sup>22</sup> with a Tesla BM 208 voltage supply applying the voltage gradient of approximately  $15 \text{ V cm}^{-1}$ . Tetraethylammonium iodide served as the mobility standard, starch and antipyrine as the electroosmosis standards for  $\text{pH} < 3$  and  $\text{pH} > 3$ , respectively. All experiments were carried out at the temperature  $20^\circ\text{C}$ ; chromatographic paper Whatman No 2 was employed. The hydrogen ion concentration was adjusted for the electrophoretic measurements as follows:  $\text{pH} \sim 1$  with  $0.1\text{M-HNO}_3$ ,  $\text{pH} 1.8-2.4$  with monochloroacetic acid,  $\text{pH} 7$  with sodium barbiturate, and  $\text{pH} \sim 13$  with  $0.1\text{M-KOH}$ .

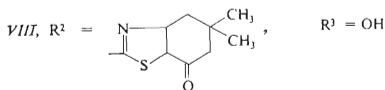
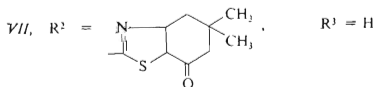
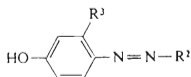
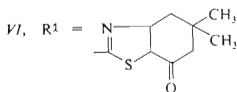
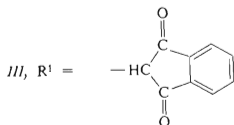
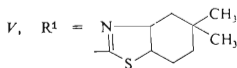
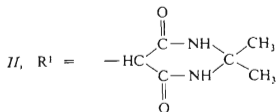
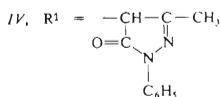
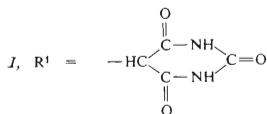
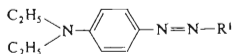
## RESULTS AND DISCUSSION

The series of the azo compounds *I-VIII* was synthesized and studied with a view to establishing the relation between structure of azo compounds and their acid-base properties and reduction mechanism.

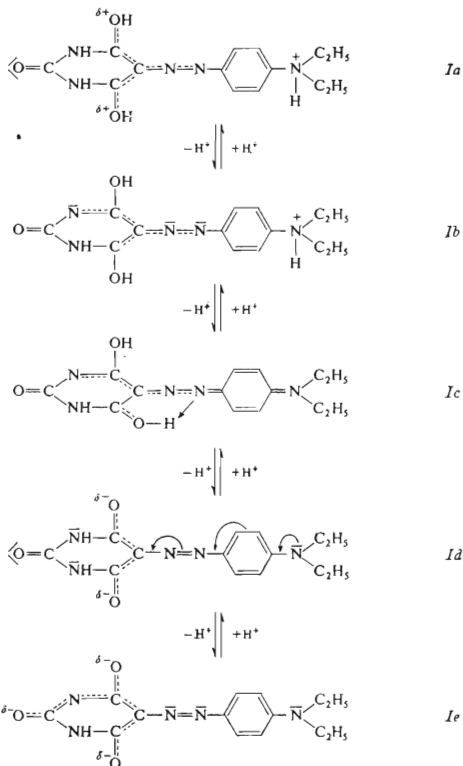
The acid-base equilibria of the compounds were studied spectrophotometrically. Their oxidation-reduction properties and their reduction products were investigated by preparative electroreduction, whose course was monitored spectrophotometrically and polarographically.

The absorption curves of the aqueous-alcoholic solutions of the compound *I* for different pH values exhibit four isosbestic points, indicating the occurrence of four acid-base equilibria; the equilibria are reversible. The first of them, between the species *Ia* and *Ib*, appears in solutions of  $7\text{M}$  to  $0.1\text{M-HClO}_2$ . The two species involved are capable of existence even in a solution free of the organic solvent. The electrophoretic measurements evidenced the presence of a positive charge at the compound *I* in solution pH 3, hence a protonized nature of the *Ib* species. Its absorption maximum (Table I) is shifted towards higher wavenumbers as compared with the species *Ia*; the shift is considerably lower than that observed in the analogous systems *IIIb-IIIa* or *IVb-IVa*. In the pH 1-7 region, equilibrium between the *Ib* and *Ic* forms is observed. Electrophoretic measurements in neutral solutions proved that a molecule of the *Ic* species does not possess any charge. The appreciable shift of the absorption band towards lower wavenumbers indicates the formation

of a *p*-quinoid electron distribution. Equilibria between the *Ic* and *Id* species and between the *Id* and *Ie* species are observed at pH 7–10.5 and at pH > 10.5, respectively. The *Id* and *Ie* species, unlike the *Ic* form, are again capable of existence in solution even without addition of the organic solvent. Even the *Id* form possesses a negative charge, as found by electrophoretic measurements. The direction, in which the



absorption bands of the *Ic*, *Id*, *Ie* forms are shifted, indicates that the *p*-quinoid electronic structure vanishes.



The study of the acid-base equilibria of the substances *II–IV* led to analogous results, except for the doubly dissociated *e* species. The results of measurements summarized in Table I, suggest the following interpretation. The fundamental, electroneutral form of the azo compounds *I–IV* is the *c* form. Its red colour indicates

the quinoid electron distribution in the molecule. A hydrogen atom at the  $\alpha$ -carbon of the keto compound would not permit such an electron distribution to occur. A rearrangement of the hydrogen in the case in question is feasible only if the enol form is created. The assumption of a tautomeric equilibrium is corroborated by the fact that when a series of equimolar solutions of the azo compound *III* or *IV* of different acidities were prepared by mixing the acidic (pH  $\sim$  2) and neutral solutions and allowed to reach the equilibrium temperature, their absorption curves did not intersect in an isosbestic point. A sharp isosbestic point was, however, obtained when the measurements were repeated several hours later. This evidences that the equi-

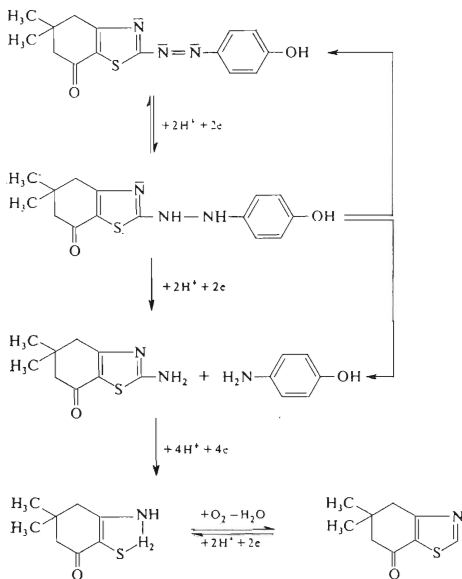
TABLE I

Characteristics of the Acid-Base Forms of the Azo Compounds *I-VI*

Species	Charge	pK	Region of existence	$\lambda_{\max}$ $\text{cm}^{-1}$	$\epsilon_{\max}$ $\text{l mol}^{-1} \text{cm}^{-1}$	Colour
<i>Ia</i>	++	—	$c_{\text{HClO}_4} > 7\text{M}$	25 700	28 700	yellow
<i>Ib</i>	+	4.67	pH 1—2	26 080	28 600	yellow
<i>Ic</i>	0	8.86	pH 6.8—7.3	19 080	27 700	red
<i>Id</i>	—	12.97	pH 10.2—11.5	20 550	22 500	orange
<i>Ie</i>	—	—	pH $>$ 13.3	25 500	18 000	yellow
				22 300	19 000	
<i>IIa</i>	++	—	$c_{\text{HClO}_4} > 6\text{M}$	25 250	22 500	yellow
<i>IIb</i>	+	4.55	pH 1—2	26 250	22 370	yellow
<i>IIc</i>	0	10.75	pH 7—8.5	19 000	28 500	red
<i>IId</i>	—	—	pH $>$ 12.5	25 500	19 750	yellow
<i>IIIa</i>	++	—	$c_{\text{HClO}_4} > 7\text{M}$	23 800	29 750	yellow
<i>IIIb</i>	+	5.01	pH 1—3	25 350	29 400	yellow
<i>IIIc</i>	0	9.35	pH 7—7.3	17 800	28 450	wine red
<i>IIId</i>	—	—	pH $>$ 12.5	21 350	28 000	orange
<i>IVa</i>	++	—	$c_{\text{HClO}_4} > 7\text{M}$	24 450	22 500	yellow
<i>IVb</i>	+	4.74	pH 1—2.5	25 740	27 750	yellow
<i>IVc</i>	0	9.96	pH 7.5—8	18 900	28 000	red
<i>IVd</i>	—	—	pH $>$ 12.5	22 400	29 000	yellow
<i>Va</i>	++	—	$c_{\text{HClO}_4} > 5\text{M}$	24 500	17 600	yellow
<i>Vb</i>	+	2.97	pH 1	16 500	48 000	blue
<i>Vc</i>	0	nondiss.	pH $>$ 7	19 200	41 000	red
<i>VIa<sup>a</sup></i>	++	—	$c_{\text{HClO}_4} > 6\text{M}$	21 900	45 500	yellow
<i>VIb<sup>a</sup></i>	+	—	$c_{\text{HClO}_4} = 0.5\text{M}$	16 900	62 000	blue
<i>VIc</i>	0	keto	pH 3—13	17 200	61 000	blue
<i>VI<sup>d</sup></i>	0	enol	$c_{\text{NaOH}} > 2\text{M}$	17 500	60 000	blue

<sup>a</sup> Ref.<sup>14</sup>.

librium between the *IIIb* and *IIIc* forms, or *IVb* and *IVc* forms, does not establish instantly, as would correspond to a simple acid-base equilibrium; the rather slow process is in accordance with the concept of a tautomeric conversion. A lowering of the acidity brings about formation of the *d* species. As a result of the electron donor effect of the anion, operating against the effect of the diethylamino group, the *p*-quinoid electron distribution vanishes, which is manifested by the shift of the absorption band towards higher wavenumbers. Acidification of the electroneutral *c*



species brings about the occurrence of a positive charge at the molecule. The *b* species is yellow, so the protonation is obviously associated with vanishing quinoid electron distribution; the nitrogen atom of the diethylamino group must be involved in the protonation. Additional increase in acidity leads to the formation of the doubly protonized *a* species, conditioned by a partial lengthening of conjugation of the double bonds. The difference between the positions of the absorption maxima corresponding to the *a* and *b* species is higher in the case of the compounds *III* or *IV* than in the case of the compounds *I* or *II*. This can be explained so that the second

protonation of the substances *I–IV* proceeds *via* the oxygen atom of the carbonyl group and compels the formation of the protonized enol form, a system with a higher degree of conjugation than the keto form. The singly protonized *b* species exist in keto–enol tautomeric equilibria, shifted more in favour of the keto form in the case of the compounds *III* and *IV*. This concept is consistent with the reported behaviour of 1,3-indanedione, dimedone, and barbituric acid. Infrared spectroscopic studies proved<sup>23,24</sup> that solid dimedone exists in the enol form stabilized by strong intermolecular forces, whereas 1,3-indanedione in the solid state as well as in chloroform solutions exists in the diketo form. A comparison of the dissociation constants of the *Iib* ( $pK = 4.55$ ) and *Iic* ( $pK = 10.75$ ) forms with those of the analogous *IIIb* ( $pK = 5.01$ ) and *IIIc* ( $pK = 9.35$ ) forms does not contradict the concept of a more stable enol form of the substance *II*. The IR and NMR study of the acid–base species of barbituric acid and its N- or C-substituted methyl and halogen derivatives has confirmed that the protonized form of barbituric acid is the enol form, the positive charge being uniformly distributed over the molecule. The assumption of the protonized enol form of the indanedione system is in agreement with the results of NMR study of 2-substituted 1,3-indanedione derivatives<sup>25</sup>.

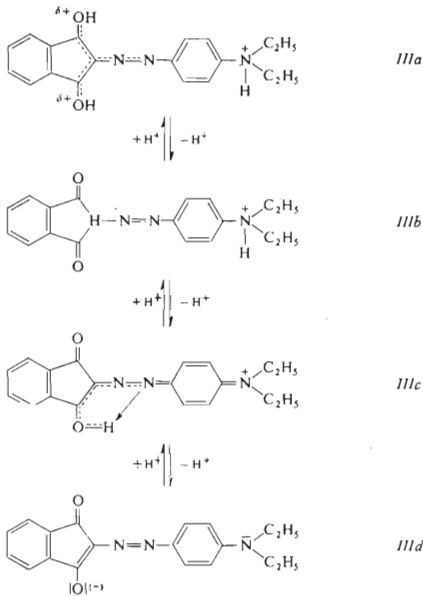
The acid–base species of the azo compounds *II*, *III* and *IV* can be described analogously (except for the *e* species).

The azo compound *V* has been studied in more detail. It exists in neutral or alkaline solutions in the fundamental, red electroneutral *Vc* form, and is completely protonized only at pH 1; the occurrence of a positive charge was confirmed by electrophoretic measurements. The absorption band of the blue, singly protonized *Vb* form is shifted towards lower wavenumbers in comparison with that of the *Vc* form. Thus protonation of the compound *V*, unlike the substances *I–IV*, contributes further to the *p*-quinoid electron distribution in the molecule. In strongly acidic solutions ( $5M-H_2SO_4$ ) the molecule occurs as the double protonized *Va* species. The second protonation, by virtue of which the *p*-quinoid electron distribution disappears, must occur at the nitrogen atom of the diethylamino group.

The results of spectrophotometric study of the azo compounds *I–VI* are summarized in Table I. The acid–base equilibria of the substances *VII* and *VIII* are the subject of the work<sup>16</sup>. The data in Table I lead to the conclusion that the first protonation of the compounds *I–IV* proceeds *via* the nitrogen atom of the diethylamino group, that of the compounds *V–VIII* *via* the hetero nitrogen of the thiazole ring, the diethylamino group (in the former case) being more basic than the hetero nitrogen (in the latter case). The compound *VI*, unlike *V*, exhibits a more pronounced *p*-quinoid electron distribution in the electroneutral form, due to the conjugation with the carbonyl group. The non-dissociated hydroxy group of the substance *VII*, in contrast to the diethylamino group of the substance *VI*, is not capable of compelling the quinoid electron distribution; the latter takes place only after its dissociation, or protonation of the thiazole ring nitrogen.

All the azo compounds studied, except *VI*, can be used as acid–base indicators. The substances *I–IV* can be employed conveniently as two-transition indicators, allowing strong and weak acids to be separately determined<sup>17</sup>.

The azo compounds *I–VIII* were subjected to preparative electroreduction in acidic and alkaline media in order to identify and examine their properties. The course of the preparative electroreduction as well as the behaviour of the first-step reduction products is very similar for the compounds *I–IV* and can be well demonstrated on the substance *III*.



The course of preparative electroreduction of the compound *III* in acidic solution at a controlled potential from the range of limiting current corresponding to the first of the three cathodic waves was monitored polarographically and spectrophotometrically. As the former method showed, the first wave decreased and vanished, while the positions and heights of the second and the third waves remained constant. This evidences not only that the first-step reduction actually occurred, but also that



its product — in acidic solution and inert atmosphere — at the end of the reduction was the same as that formed during the mercury drop life. In the spectra (Fig. 1) an isosbestic point is found at  $41320\text{ cm}^{-1}$ , indicating that a single (or at least apparently single) equilibrium takes place. From the fact that this equilibrium was irreversible and from the relative height of the first cathodic wave of the compound *III* it could be inferred that the reaction product was an equimolar mixture of the corresponding amines.

In order to identify directly one of the products of the first-step reduction of the compound *III*, we applied the preparative electroreduction to 2-isonitroso-1,3-indanedione, which is known<sup>26</sup> to yield 2-amino-1,3-indanedione on the first-step reduction. Based on a comparison of the record in Fig. 1 with the record of the first-step reduction of 2-nitroso-1,3-indanedione it could be proved that one of the two reaction products of the compound *III* was 2-amino-1,3-indanedione ( $\tilde{\nu}_{\text{max}} = 43400\text{ cm}^{-1}$ ,  $\epsilon_{\text{max}} = 34500\text{ l mol}^{-1}\text{ cm}^{-1}$ ). In acidic solution it is relatively stable; it remains steady at least during the preparative electroreduction (about 3 h), as borne out by the occurrence of the isosbestic point. Hydrolytic degradation of the amino group in acidic solution, in paper<sup>27</sup> inferred from the infrared spectra, can only be observed after a longer standing of the solution or during the isolation of the product from the acidic solution. A simple redox equilibrium between 2-isonitroso-1,3-indanedione and 2-amino-1,3-indanedione is observed in inert atmosphere even in weakly acidic solutions (Fig. 2), which disagrees with the interpretation of results in<sup>26</sup>, assuming a reaction between the two compounds associated with the formation of Ruheman's purple.

In alkaline solutions and inert atmosphere, 2-amino-1,3-indanedione (*X*) is also stable — a simple oxidation-reduction equilibrium occurs ( $\tilde{\nu}_{\text{isosb}} = 35910\text{ cm}^{-1}$ ). In this system, the compound readily undergoes oxidation ( $E_{1/2} = 3.25\text{ V (S.C.E.)}$ ) and rapid atmospheric oxidation (Fig. 3). During the latter, its loss is first associated with a relative increase in the concentration of the product with  $\tilde{\nu}_{\text{max}} = 43100\text{ cm}^{-1}$ , which in alkaline solution is also unstable. Therefore we monitored the atmospheric oxidation of the compound *X* also in weakly acidic solution (Fig. 4), and compared it with the behaviour of ninhydrine (*XI*). The latter retains its absorption band position,  $\tilde{\nu}_{\text{max}} = 43100\text{ cm}^{-1}$ , over the entire region pH 1–13; in acidic and neutral solutions it is steady, in alkaline solutions it undergoes changes (Fig. 5).

Fig. 3 suggests that in alkaline solutions, the compound *X* is oxidized by atmospheric oxygen rather rapidly to give 2-imino-1,3-indanedione, which in turn hydrolyses very rapidly (virtually instantly) to *XI*. The latter undergoes changes, described in<sup>28</sup>, with a rate comparable to that of oxidation of *X*. In weakly acidic solutions, however, where *XI* is steady, the atmospheric oxidation of *X* does not represent a single equilibrium (Fig. 4), as *XI* or 2-imino-1,3-indanedione react with the (unoxidized) *X* to give the products reported in paper<sup>27</sup>.

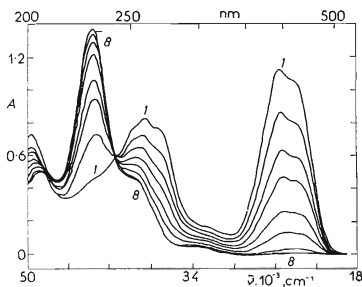


FIG. 1

Spectrophotometric Monitoring of the Preparative Electroreduction of the Compound *III* in Acidic Solution at a Potential from the Region of Beginning of the Limiting Current of the First Cathodic Wave

$c_{III} = 4 \cdot 10^{-5} \text{ mol l}^{-1}$ , 40% (v/v) ethanol,  $E = -0.4 \text{ V (s.c.e.)}$ ,  $d = 1 \text{ cm}$ . 1 Before the reduction, 2–7 during reduction, 8 after reduction.

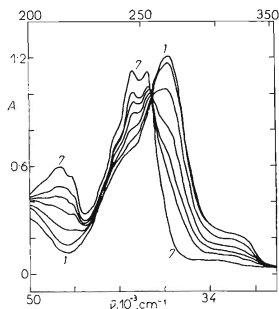


FIG. 2

Spectrophotometric Monitoring of the Preparative Electroreduction of 2-Isonitroso-1,3-indanedione (*IX*) in Weakly Acidic Solution at a Potential from the Region of Beginning of the Limiting Current of the First Wave

$c_{IX} = 4 \cdot 10^{-5} \text{ mol l}^{-1}$ , 40% (v/v) ethanol,  $c_{H_2SO_4} = 2.5 \cdot 10^{-4} \text{ mol l}^{-1}$ ,  $c_{Na_2SO_4} = 5 \cdot 10^{-2} \text{ mol l}^{-1}$ ,  $d = 1 \text{ cm}$ ,  $E = -0.2 \text{ V (s.c.e.)}$ . 1 Before reduction, 2–6 during reduction, 7 after reduction.

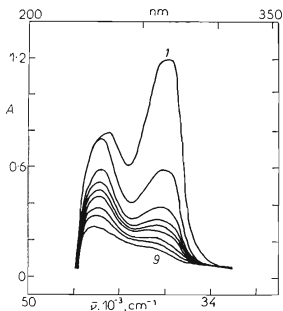


FIG. 3

Spectrophotometric Monitoring of Atmospheric Oxidation of 2-Amino-1,3-indanedione (*X*) in Alkaline Solution

$c_X = 4 \cdot 10^{-5} \text{ mol l}^{-1}$ ,  $c_{NaOH} = 5 \cdot 10^{-2} \text{ mol l}^{-1}$ , 40% (v/v) ethanol,  $d = 1 \text{ cm}$ . 1 Before oxidation, 2–8 during oxidation, 9 after 60 minutes' standing on air.

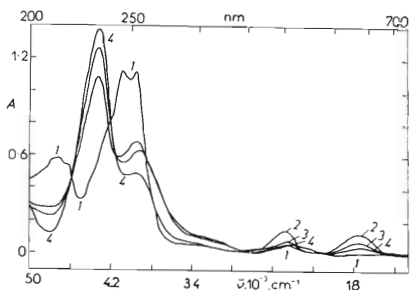


FIG. 4

Spectrophotometric Monitoring of Atmospheric Oxidation of 2-Amino-1,3-indanedione (*X*) in Weakly Acidic Solution

$c_X = 4 \cdot 10^{-5} \text{ mol l}^{-1}$ ,  $c_{\text{H}_2\text{SO}_4} = 2.5 \cdot 10^{-4} \text{ mol l}^{-1}$ , 40% (v/v) ethanol,  $d = 1 \text{ cm}$ . 1 Before oxidation, 2 and 3 during oxidation, 4 after oxidation.

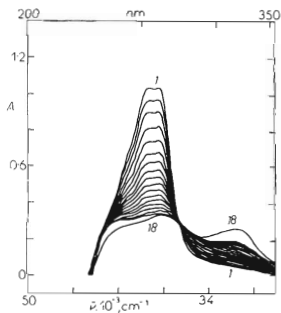


FIG. 5

Spectrophotometric Monitoring of the Behaviour of Ninhydrine (*XI*) in Alkaline Solution in Dependence on Time

$c_{\text{XI}} = 4 \cdot 10^{-5} \text{ mol l}^{-1}$ ,  $c_{\text{NaOH}} = 5 \cdot 10^{-2} \text{ mol l}^{-1}$ , 40% (v/v) ethanol,  $d = 1 \text{ cm}$ . 1 0 min, 2–11 in 2 min intervals 12 after, 30 min, 13 after 60 min.

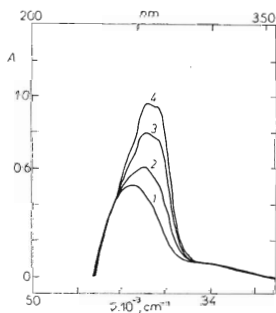


FIG. 6

Spectrophotometric Monitoring of the First Step of Oxidation of *p*-N,N-Diethylamino-phenylenediamine (*XII*) in Alkaline Solution

$c_{\text{XII}} = 6 \cdot 10^{-5} \text{ mol l}^{-1}$ ,  $c_{\text{NaOH}} = 5 \cdot 10^{-2} \text{ mol l}^{-1}$ ,  $d = 1 \text{ cm}$ . 1 Before oxidation, or during a 15 min standing on air, 2 after 17 min, 3 after 19 min, 4 after 21 min standing on air.

The described behaviour of the compound *X*, obtained by the first-step reduction of 2-isonitroso-1,3-indanedione, is observed also in the case of the product of first-step reduction of the compound *III*. A spectrophotometric examination of the changes, however, is in this case rather difficult because the other reduction product, *p*-*N,N*-diethylaminophenylenediamine (*XII*), being stable in acidic solutions ( $\bar{\nu}_{\max} = 49000 \text{ cm}^{-1}$ ,  $\epsilon_{\max} = 4000 \text{ l mol}^{-1} \text{ cm}^{-1}$ ), in alkaline solutions and under air is subject to conversions (Figs 6 and 7).

The mechanism of oxidation of *p*-phenylenediamine type compounds is treated in papers<sup>29-31</sup>. The changes (Figs 6 and 7), observable only if the experimental conditions are adhered to, were utilized to prove the existence of *XII* among the products of the first-step reduction of the compounds *I-IV*. Spectrophotometric characteristics of the amino compounds formed as a result of the reduction are given in Table II.

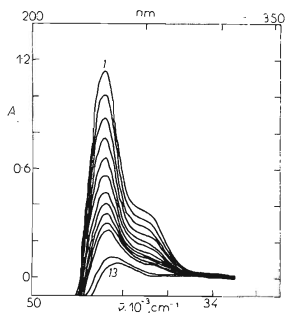


FIG. 7

Spectrophotometric Monitoring of the Second Step of Oxidation of *p*-*N,N*-Diethylaminophenylenediamine (*XII*) in Alkaline Solution

Experimental conditions as for Fig. 6. 1 After 22 min standing on air, 2-11 in 5 min intervals, 13 after 150 min standing.

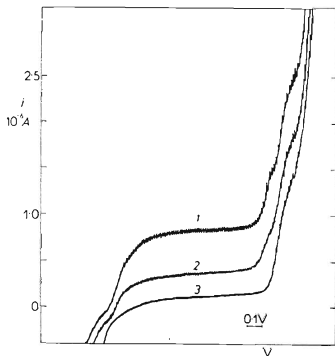


FIG. 8

Polarographic Monitoring of the Preparative Electroreduction of the Compound *VII* in Acidic Solution at a Potential from the Beginning of the Limiting Current of the First Cathodic Wave

$c_{VII} = 1 \cdot 10^{-4} \text{ mol l}^{-1}$ ,  $c_{H_2SO_4} = 5 \cdot 10^{-2} \text{ mol l}^{-1}$ , 40% (v/v) ethanol,  $E = -0.2 \text{ V (s.c.e.)}$ , OH-102 instrument, gain  $4 \cdot 10^{-8} \text{ A/d}$ ,  $0.1 \text{ V/cm}$ , start from  $0 \text{ V (s.c.e.)}$ ,  $t_{drop} = 3 \text{ s}$ . 1 Before reduction, 2 during oxidation, 3 after reduction.

Comparing the polarographic behaviour of the azo compounds *V–VIII* with that of the compounds *I–IV* we found the height of the first cathodic wave for the former group to be half of that for the latter group over the whole pH region. In the case of the compounds *V–VIII* a hydrazo compound is formed on the mercury drop, not undergoing disproportionation during the drop life (about 3 s).

The azo compound *V* exhibits a single cathodic wave, the compounds *VI–VIII* give rise to three cathodic waves. Thus the primary product of the two-electron reduction of the substance *V* is polarographically further irreducible unlike the primary products of the two-electron reduction of the substances *VI–VIII*, which are further reducible in two additional steps.

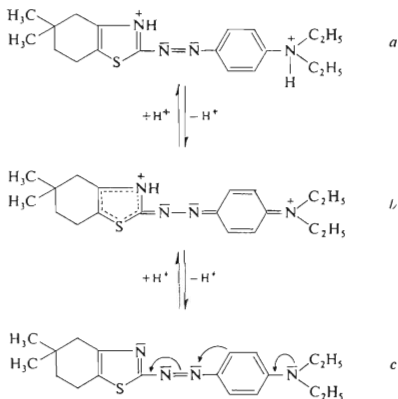
The spectrophotometric record of the preparative electroreduction for the compound *V* in acidic solution displays chaotically intersecting absorption curves. During the examination of a sample taken during the electroreduction, we found that the band with  $\tilde{\nu}_{\max} = 16500 \text{ cm}^{-1}$ , corresponding to the *Vb* species, increased with time even under inert conditions. When the samples taken during the reduction were allowed to stand in inert atmosphere for approximately 4 h, their absorption curves intersected in a sharp isosbestic point. Comparing the spectra of the corresponding amines we were able to prove that the established equilibrium was one

TABLE II

Spectrophotometric Characteristics of the Amino Compounds Formed by Reduction of the Azo Compounds *I–VI*

Amino compound	pH	$\lambda_{\max}$ $\text{cm}^{-1}$	$\epsilon_{\max}$ $\text{l mol}^{-1} \text{cm}^{-1}$
Aminobarbituric acid	1	39 200	17 400
	13	34 800	13 300
2-Amino-1,1-dimethyl-3,5-cyclohexanedione	1	39 350	13 600
	13	31 000	15 400
2-Amino-1,3-indanedione	1	43 000	34 000
	13	38 000	31 500
2-Amino-1-phenyl-3-methyl-5-pyrazolone	1	41 800	11 500
	13	39 900	24 000
N,N-Diethyl- <i>p</i> -phenylenediamine	1	49 000	4 000
	13	39 100	9 600
2-Amino-5,5-dimethyl-4,5,6,7-tetrahydrobenzthiazole	1	45 000	9 600
		37 400	8 000
2-Amino-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzthiazole	1	33 700	14 300
	13	27 400	19 700

between the azo compound and the corresponding amines. In this manner we proved that the primary product of reduction of the azo compound *V* is not associated with a decomposition of the molecule, and that, being polarographically irreducible, it undergoes disproportionation to the azo compound and the corresponding amines. The rate of disproportionation is low as compared with the mercury drop time, but too high to allow the hydrazo compounds to be obtained by preparative electroreduction.



The azo compound *VII* in acidic medium reduces polarographically in three distinctly separated cathodic waves. The polarographic record of its preparative electroreduction at a controlled potential from the region of the beginning of the limiting current corresponding to the first cathodic wave (Fig. 8) shows that, although the reduction was conducted at a potential that did not allow the compound *VII* to be reduced to the second step, not only the first, but also the second wave of the compound vanishes. From the spectrophotometric examination, the same conclusion can be drawn as in the case of the compound *V*.

The first step of reduction of the azo compound *VII* leads to the hydrazo compound, which undergoes disproportionation, but which is also polarographically reducible to the corresponding amines. The third cathodic wave corresponds to the reduction of 2-amino-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzthiazole, whose reduction mechanism has been described in<sup>21</sup>.

The mechanism of the polarographic reduction of the azo compound *VII* can be described by the following scheme.

The mechanism of the polarographic reduction of the compounds VI and VIII is analogous; the rate of disproportionation of the corresponding hydrazo compounds, however, is substantially different.

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