829. *The Polarography of* 4-*Arylazo*-1-*naphthylamines.*

By A. G. CATCHPOLE and R. A. KNAUST.

A plot of the half-wave potentials of 4-(*para*-substituted arylazo)-1-naphthylamines in solutions at four pH's against Hammett's σ-function is essentially linear. The reduction is favoured by a lower pH and the slopes of the lines show that electron-attracting groups favour reduction, but only to a relatively small extent, and that this effect is less as the acidity is increased.

THE polarographic behaviour of azo-compounds has been reported by several workers,[1] *e.g.*, of azobenzene, 4-aminoazobenzene, 4-dimethylaminoazobenzene, 4-methoxyazobenzene, and 4-acetoxyazobenzene, as well as some azo-dyes. The half-wave potentials of these substances have been determined at various pH values, at different concentrations, and with different configurations at the azo-link but, so far, the variation of the half-wave potential with substitution in azo-compounds has not been reported. This has now been investigated for a series of 4-(*para*-substituted arylazo)-1-naphthylamines.

Tachi and Shikata [2] found that the reduction potential of 4-dimethylaminoazobenzene was more negative than that of the unsubstituted amino-derivative, which suggests that the reduction is hindered by increasing electron-release from the substituent. This is supported by Pittoni [3] who reported a half-wave potential for azobenzene of —0·80 v and for 4-dimethylaminoazobenzene of —0·88 v, and by Vladimirtsev and Poskovskii [4] who obtained half-wave potentials for azobenzene —0·320 v, and the 4-acetoxy- —0·322 v, 4-methoxy- —0·358 v, and 4-hydroxy-derivative —0·383 v.

Laitinen and Kneip [5] obtained half-wave potentials for 4-dimethylaminoazobenzene which became less negative with decreasing pH. They reported that at low pH the reaction involved a four-electron reduction but at pH 9·5 and 13·5 a two-electron reduction to the unstable hydrazo-compound.

Experimental.—4-*Arylazo*-1-*naphthylamines.* The azo-compounds were prepared from the anilines by diazotisation and coupling with 1-naphthylamine, followed by recrystallisation to constant m. p.

Measurements.—These were made on a Tinsley model 18/1M polarograph with the sensitivity

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[1] Kolthoff and Lingame, " Polarography," Interscience, New York, 2nd edn., p. 767.
[2] Tachi and Shikata, *Mem. Coll. Agric. Kyoto*, 1937, **40**, 1.
[3] Pittoni, *Atti Soc. med. chir. Padova*, 1947, **25**, 125.
[4] Vladimirtsev and Poskovskii, *Doklady Akad. Nauk S.S.S.R.*, 1952, **83**, 855.
[5] Laitinen and Kneip, *J. Amer. Chem. Soc.*, 1956, **78**, 736.

control adjusted to give a full-scale deflection with a current of 2 microamperes. For 4-*p*-nitrophenylazo-1-naphthylamine, owing to its low solubility, the sensitivity was adjusted to give a full-scale deflection with a current of 0·5 microampere. The temperature was controlled at 25° ± 0·1°. The values of the constants of the electrode, determined in aqueous 0·1M-chloride at zero applied potential and a head of mercury of 41·8 cm., were: $t = 3{\cdot}45$ sec., $m = 2{\cdot}66$ mg. sec.$^{-1}$.

The solvent was 50% v/v aqueous ethyl alcohol, and each solution contained 0·02% w/v of polyvinyl alcohol as a maximum suppressor and was 10^{-4}M in azo-compound, except for the nitro-compound whose exact concentration was unknown (owing to its low solubility).

The following concentrations of base electrolyte were used, the apparent pH of the solution as measured by a glass electrode being shown in parentheses: 0·1M-$NaHSO_4$, 0·01M-Na_2SO_4 (2·0); 0·05M-$NH_4H_2PO_4$ (5·1); 0·05M-$(NH_4)_2HPO_4$ (8·2); and 0·05M-NaOH, 0·05M-KCl (12·7). No maxima were observed in any of these solutions with any of the compounds.

The results are tabulated.

Polarographic reduction of 4-(para-*substituted arylazo*)-1-*naphthylamines.*

Subst.	$E_{\frac{1}{2}}$ (v) *v.* S.C.E.				
pH:	2·0	5·1	8·2	12·7	M. p.
MeO	−0·051	−0·455	−0·62	−0·866	124·5°
Me	−0·038	−0·429	−0·582	−0·828	147·5
H	−0·029	−0·410	−0·544	−0·811	123
Cl	−0·035	−0·389	−0·549	−0·794	189
Br	−0·039	−0·381	−0·545	−0·793	200
MeO_2C	−0·024	−0·366	−0·490	—	192
Ac	−0·061	−0·308	−0·475	−0·750	215
NO_2	−0·022	−0·300	−0·452	−0·675	256 (decomp.)

Discussion.—In acid solution amino-substituted azo-compounds are protonated and there is considerable evidence that in many cases the proton is taken up by the nitrogen atoms of the azo-linkage,[6] there being an equilibrium $^+H_3N\cdot X\cdot N_2\cdot Y \rightleftharpoons H_2N\cdot X\cdot N{=}NH^+\cdot Y$. Both structures, being positively charged, would be expected to increase the electron-affinity of the azo-linkage. In solutions of lower pH the concentrations of molecules with these structures will increase and the half-wave potentials would be expected to become less negative as the pH decreases. For 4-dimethylaminoazobenzene Laitinen and Kneip [5] reported changes in the value of $E_{\frac{1}{2}}$ of about 0·108 v per pH unit below pH 6, and of 0·051 v per pH unit above pH 7. The 4-arylazo-1-naphthylamines show much the same behaviour, the $E_{\frac{1}{2}}$ values becoming less negative over the pH range 5·1—2·0 by amounts which varied with the compound, from 0·13 v per pH unit for those with electron-releasing substituents to 0·99 v for those with electron-attracting substituents. As with *p*-dimethylaminoazobenzene the change per pH unit in solutions of higher pH is less, varying from 0·058 to 0·049 v per pH unit over the pH range 5·1—12·7.

The results further show that at a fixed pH the $E_{\frac{1}{2}}$ values become increasingly less negative as the electron-attracting power of the *para*-substituent increases. This is consistent with the results mentioned previously and indicates that the substituents cause permanent electron-displacements at the azo-linkage with resulting changes in the electron-affinity of the molecule, this affinity being increased by electron-attracting and decreased by electron-releasing groups. Measured in this way the electron-density of the azo-linkage decreases in the order shown in the Table. This is the same as was found by Badger and Lewis [7] from measurements of the rate of oxidation of azobenzenes by perbenzoic acid.

Plotting the $E_{\frac{1}{2}}$ values against the Hammett σ-function [8] for each of the substituents

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[6] Klotz, Fiess, Chen Ho, and Mellody, *J. Amer. Chem. Soc.*, 1954, **76**, 5136; Rogers, Campbell, and Maatman, *ibid.*, 1951, **73**, 5122; Cilento, Miller, and Miller, *ibid.*, 1956, **78**, 1718; McGuire and Zeffanti, *J. Org. Chem.*, 1956, **21**, 632; Jaffé and Si-Jung Yeh, *ibid.*, 1957, **22**, 1281; Sawicki, *ibid.*, p. 365.

[7] Badger and Lewis, *J.*, 1953, 2147.

[8] McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420.

gives a straight line at each of the four pH values. The methoxycarbonyl is hydrolysed in the strongly alkaline solution, and under these conditions the value for $E_{\frac{1}{2}}$ was unreliable. The slopes of the lines at the pH values of 5·1, 8·2, and 12·7 are practically the same, at about 0·10 v per Hammett unit, and indicate a weak substituent influence. At pH 2·0 the slope is only about 0·03 v per Hammett unit, indicating that the substituent influence is weaker still under these conditions. In the protonated forms of the arylazo-1-naphthylamines the positive charge will, no doubt, have a dominating effect on the electron-affinity of the molecule, facilitating the reduction but decreasing the substituent influence. Both the protonated structures shown above, particularly the $-N{=}NH^{+}-$ form where there is a full positive charge at the seat of reduction, could account for the large shift in $E_{\frac{1}{2}}$ to less negative values observed as the medium becomes more strongly acidic.

The $E_{\frac{1}{2}}$ values obtained for unsubstituted phenylazo-1-naphthylamine agree with those obtained by Laitinen and Kneip [5] for *p*-dimethylaminoazobenzene at the same pH. The slightly more negative values for the latter compound reflect the greater electron-releasing power of the dimethylamino-group than of the amino-group. This suggests that molecules of a similar structure are undergoing reduction in the two cases and discounts the possibility that an imino-form $HN{:}X{:}N{\cdot}NH{\cdot}Y$ is involved (such tautomerism is impossible for *p*-dimethylaminoazobenzene).

For *p*-dimethylaminoazobenzene and phenylazo-1-naphthylamine differences appear, however, when the reversibility of the reduction is considered. For azobenzene Castor and Saylor [9] reported reduction as reversible over the whole of the pH range covered in the present investigation, whereas Wawzonek and Fredierickson [10] found reversibility only over the pH range 2—6. Using the equation

$$E = E_{\frac{1}{2}} + 2{\cdot}3\frac{\boldsymbol{R}T}{n\boldsymbol{F}}\log_{10}\frac{i}{i_d - i}$$

and plotting E against $\log_{10}[i/(i_d - i)]$ gives straight lines for all the arylazo-1-naphthylamines at the lower pH's but not for those compounds with electron-releasing substituents at pH 12·7 or for the *p*-nitro-compound at pH 8·2. The non-linear plots are taken as evidence of irreversibility under these conditions. The linear plots obtained at the lower pH's are not, of themselves, evidence of reversibility but, in view of the other evidence, it is reasonable to assume reversibility with the arylazo-1-naphthylamines at the lower pH's. This assumption being made, it becomes of interest to calculate the number of electrons involved in the reduction from the slopes of the linear plots at the lower pH's. Castor and Saylor [9] reported a two-electron reduction with azobenzene, but Laitinen and Kneip [5] found four electrons to be involved in the reduction of *p*-dimethylaminoazobenzene in acid solution. Values of about 2 are obtained with the arylazo-1-naphthylamines, though, in the absence of more definite evidence that the reactions are reversible, these values must be treated with reserve.

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[9] Castor and Saylor, *J. Amer. Chem. Soc.*, 1953, **75**, 1427.
[10] Wawzonek and Fredierickson, *J. Amer. Chem. Soc.*, 1955, **77**, 3985.