Tetrahedron. Vol. 26, pp. 1771–1775. Pergamon Press 1970. Printed in Great Britain

POLAROGRAPHIC CHARACTERIZATION OF THE DIMERIC REARRANGEMENT PRODUCTS FORMED FROM 4-NITROPHENYL-ACETATE ION IN BASIC SOLUTION

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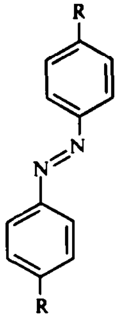
(*Received in the UK* 26 *October* 1969; *Accepted for publication* 5 *December* 1969)

Abstract—The structures of the products derived from the reaction of aqueous methanolic alkali with 4-nitrophenylacetic acid were determined by polarographic techniques. Comparison was made between their half-wave potentials and those of azo- and azoxybenzene derivatives, which showed that the products were 4,4′-dioxaloazobenzene and 4,4′-dioxaloazoxybenzene.

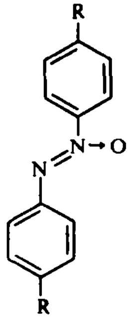
CHARACTERIZATION of organic compounds is one of the uses to which polarography can be put, as described by Zuman[1, 2] and illustrated in his analysis of the structure of the so-called phenylthiohydantoic acid.[3] The method consists of comparing half-wave potentials for reduction or oxidation of electroactive groups in the unknown compound with those for similar groups in known compounds. For valid comparisons the electrolysis mechanism must be the same. Determination of the number of electrons (n) involved in the process can be helpful, as can a study of the pH dependence of the half-wave potential. The effect of substituents on the half-wave potential can be correlated by the modified Hammett–Taft equation[4–6]

$$\Delta E_{\frac{1}{2}} = \rho \cdot \sigma$$

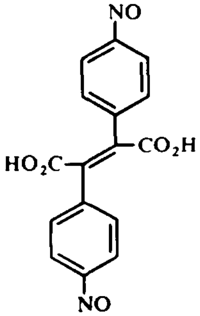
When 4-nitrophenylacetic acid was heated in solution in aqueous methanolic alkali, a material was isolated whose preliminary elemental analysis and spectral data were consistent with its being either I, II or III ($R = CO.CO_2H$)[7].



I



II



III

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DISCUSSION

Assuming that the two identical groups in I and II or the two nitroso groups in III are reduced simultaneously—i.e. at the same potential, I should give two polarographic reduction waves, one for the azo group corresponding to two electrons, the other for the two carbonyl groups, analogous to phenylglyoxylic acid, $C_6H_5.CO.CO_2H$ (four electrons). II would be similar to I except that the azoxy group would give a four electron wave. The two waves from III would be for the double bond, analogous to stilbene or fumaric acid (two electrons), and for the two nitroso groups (four electrons).

TLC of the methylated material showed it to be a mixture of two compounds, A and B, which were separated by chromatography.[7]

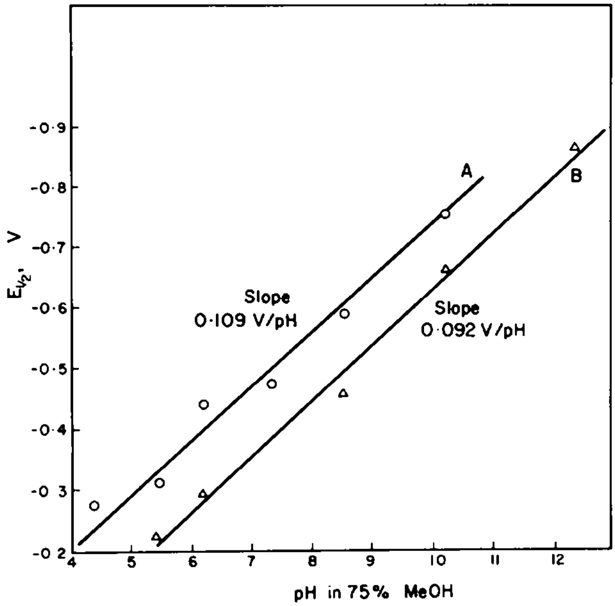

FIG. 1 Graph of $E_{\frac{1}{2}}$ vs pH in 75% MeOH for A and B.

Polarograms of A and B were run in 75% methanol owing to solubility problems. The reduction waves of each compound were shown to be diffusion controlled by the linear dependence of wave height on the square root of mercury height.[1] A gave two waves, the height of the first was half the height of the second. B gave two waves of equal height. The waves were shown to be irreversible because of the non-integral values of αn_a, determined by the relation,

$$E_{\frac{3}{4}} - E_{\frac{1}{4}} = \frac{-0{\cdot}0517^{9}}{\alpha n_a},$$

shown in the table, and by the non-linearity of plots of E against log $i_d - i/i$.

The pH dependence of the half-wave potentials of the first wave of each compound (shown in Fig. 1) were in reasonable agreement with those for azo and azoxy compounds given in the literature.[10] The first reduction step took place at considerably more positive potentials than reductions of stilbene,[8a] fumaric acid[8b] or phenylglyoxylic acid,[8c] but was more negative than the reduction of nitrosobenzene.[8d] It was thus possible to exclude the structure III for both species A and B. The linear slopes were 92 mV/pH unit for A and 109 mV/pH unit for B compared with literature values of 108 mV/pH unit for azobenzene and 110 mV/pH unit for azoxybenzene.[10]

Values of n were determined from the Ilkovic equation,

$$i_d/c = 607\ n\ D\ m\ t$$

where i_d = limiting diffusion current (μA), c = concentration (molar), D = diffusion coefficient ($cm^2\ sec^{-1}$), m = rate of flow of mercury ($mg\ sec^{-1}$), t = drop time (sec), assuming that diffusion coefficients would be similar to, perhaps slightly less than, the values observed by us under identical conditions for azo- and azoxybenzene. These n values together with those of diffusion coefficients are shown in the table and suggest that A is I ($R = CO.CO_2CH_3$) and B is II ($R = CO.CO_2CH_3$).

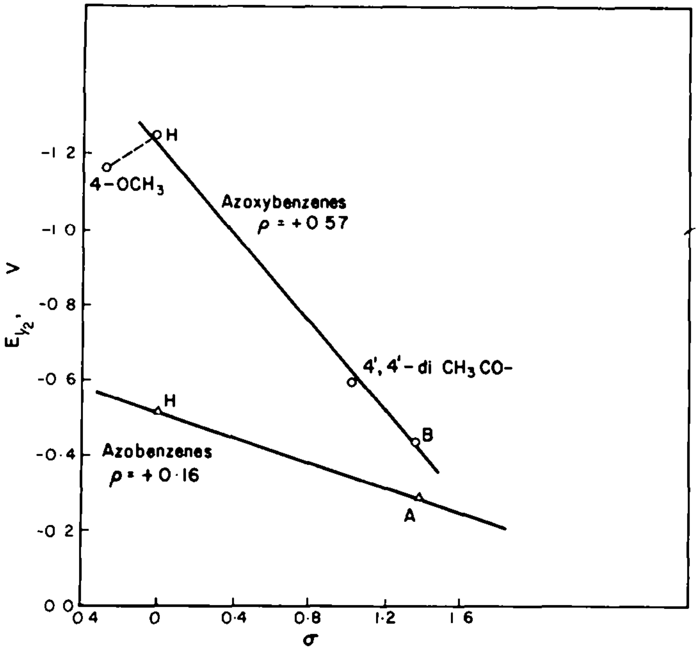

FIG. 2 Modified Hammett–Taft plot for A, B and other azo- and azoxybenzenes.

Comparison was made between half-wave potentials of A and B and those of other azo- and azoxy derivatives measured under the same conditions using the modified Hammett–Taft equation.[4–6] The ρ value for azo compounds of +0·16 given by Zuman[4] was used to construct the azobenzene line of Fig. 2. From the graph a σ value of +1·38 was obtained for the two oxalo ester groups, i.e. +0·69 for one group. The value seems reasonable as the group contains two electron withdrawing carbonyl groups. The σ value for acetyl is +0·52 and for the ethyl carboxylate +0·45.[4] It should be pointed out that the value of +0·16 V used for rho is only approximate as it is dependent on pH and the composition of the supporting electrolyte. Therefore the sigma value of +0·69 for the oxalo ester group is also only approximate as an insufficient number of points measured under our experimental conditions were used for its determination.[5]

It was more difficult to deal with the azoxy compound as maximum suppressors have marked effects on half-wave potentials.[10] Also, half-wave potentials for azoxybenzene, 4,4′-dimethoxyazobenzene and 4,4′-dichloroazoxybenzene reported in the literature[11] did not obey the linear free energy relationship. However, the values obtained by us for B, azoxybenzene and 4,4′-diacetylazoxybenzene did give a linear relation with σ as shown in Fig. 2. The slope gives a ρ value of +0·57. When a line is plotted through the value for unsubstituted azoxybenzene, the 4,4′-diacetyl derivative and the value for B using the sigma constant (approximate), the value for 4-OMe derivative shows deviation from the linear plot.

CONCLUSION

The above results indicate that A is the methyl ester of I and B is the methyl ester of II. Subsequent examination of A and B by spectroscopic methods, classical organic degradative and synthetic procedures has helped to confirm these structural assignments.[7]

TABLE. POLAROGRAMS IN 75% METHANOL CONTAINING 0·02 M ACETATE BUFFER pH 6·2 AND 0·025% METHYL CELLULOSE AT 25·0 ± 0·2° AND 1–5 × 10^{-4} M OF COMPOUND.

t = 1·88 sec
m = 2·62 mg sec^{-1}

Compound	$E_{1/2}$ (V)	i_d/C (μAM^{-1})	n	D ($\times 10^6 cm^2 sec^{-1}$)	αn_a
A	(1) −0·293	3·49	2	1·85	0·304
	(2) −1·069	7·98	4		0·282
B	(1) −0·44	8·43	4	2·72	0·246
	(2) −1·09	8·47	4		0·275
Azobenzene	−0·51	4·73	2	3·40	
Azoxybenzene	−1·25	9·55	4	3·48	
4-Azoxyanisole	−1·16	8·00	4	2·44	
4,4′-Diacetyl-Azoxybenzene	−0·60	9·5	4	3·43	

EXPERIMENTAL

Polarograms were measured on an Elliott Mk.200 polarograph at 25 ±0·2°. All potentials are given in volts *vs.* S.C.E. Preliminary results were carried out in 25% 'AR' methanol using an acetate buffer for pH 4·8, a citrate buffer for pH 7·0 and an ammonia buffer for pH 9·0. The concentration of initial material was 10^{-3} M. In all the work 0·025% methyl cellulose was added as a maximum suppressor. Polarograms of A and B were run in 75% MeOH owing to their lower solubilities and a concentrations of 1–5 × 10^{-4} M.

The variation of wave heights with mercury level was observed for A and B in acetate buffer of pH 6·2. Graphs of i_d *vs* $\sqrt{h}$ were linear for all waves.

Half-wave potentials of A and B were measured at a series of pH values, using similar buffer solns to those used for the preliminary results. These are shown in Fig. 1.

The data in Table 2 were obtained from polarograms of A, B, azobenzene, azoxybenzene, 4-azoxyanisole, and 4,4′-diacetylazoxybenzene at pH 6·2 in acetate buffer with M = 2·62 mg sec^{-1} and t = 1·88 sec (average value measured during a run).

Acknowledgement—The author wishes to thank Professor V. M. Clark, J. B. Hobbs and Dr. D. W. Hutchinson for helpful discussion and provision of materials.

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